CONTRIBUTIONS

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THEODORE LYMAN,
Director.

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THE STERILISATION OF LIQUIDS BY LIGHT OF VERY SHORT WAVE-LENGTH

By Theodore Lyman

During the past year several articles have appeared in the *Comptes rendus des Séances de l'Académie des Sciences*, Paris, on the sterilisation of liquids by ultra-violet light. The notes of M. Billon-Daguerre have particularly attracted my attention, since he has endeavored to utilise the region of the spectrum discovered by Schumann for the sterilisation of water. It is obvious that the question of the transparency of water for light of very short wave-length is important in this connection, and, as there seems to be no data which bears on the matter, I have recently made some experiments.

I used a vacuum grating spectroscope arranged in the same way as when I investigated the transparency of some solid substances. The water was distilled, but without any special precautions, and was enclosed in a cell with fluorite windows. Two of these cells were employed, one giving a water column of half a millimetre, the other giving a millimetre column. With the half-millimetre cell in the light path the spectrum was cut off at λ 1792 (Ångström units), even after a prolonged exposure. It appeared that this limit of the spectrum receded rather slowly toward the red with increase in the thickness of the water column.

As M. Billon-Daguerre wished to use light of very short wave-length, he employed a vacuum tube filled with hydrogen. This substance is known to give a strong spectrum in the region between λ 1650 and λ 1030; it must not be forgotten, however, that no lines can be ascribed to it in the region between λ 2000 and λ 1650. Thus any action due to the radiation from the vacuum tube filled with hydrogen must be confined to a layer of water so thin that light of wave-lengths shorter than λ 1650 can penetrate it.

Nature, Vol. 85, No. 2125, p. 71. July 21, 1910.

Judging from my experiments, such a layer must be very thin indeed.

Several investigators have used the mercury arc in quartz as a source of light in sterilisation experiments. There are two facts which it may be interesting to mention in this connection. In the first place, fused quartz two millimetres thick is somewhat transparent so far as λ 1500; the transparency falls off rapidly with increasing thickness. In the second place, no lines more refrangible than the strong line at λ 1850 are known in the spectrum of mercury. In this second statement my own observations are confirmed by a recent investigation of Dr. Handke.

Proceedings of the American Academy of Arts and Sciences.

Vol. XLVII. No. 21. — March, 1912.

CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY.

ON ELECTRICAL PROPERTIES OF CRYSTALS.

I. — *STRATIFICATION AND CAPACITY OF CARBORUNDUM.*

By G. W. Pierce and Rhys D. Evans.

With a Plate.

CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY.

ON ELECTRICAL PROPERTIES OF CRYSTALS.

I. STRATIFICATION AND CAPACITY OF CARBORUNDUM.

By George W. Pierce and Rhys D. Evans.

Presented by G. W. Pierce, February 14, 1912. Received February 1, 1912.

This work is a continuation of some investigations by one of us on Crystal Rectifiers for Alternating Currents.[1]

Capacity of Carborundum. — In the experiments that are described in the present paper it has been found that a fragment of carborundum, with certain attachments of the electrodes, shows a large electrostatic capacity. Measurements are given of this capacity in two typical cases.

Character of the Phenomenon. — The discussion of the measurements is followed by an account of a microscopic and electrical investigation of the carborundum, which shows that the carborundum crystal is made up of an insulating mass permeated by fine layers of conducting material. These conducting layers are nearly parallel, and, separated as they are in the crystal by non-conducting sheets, form a *natural electrical condenser*, provided electrical contacts are made to two conducting layers or sets of layers that do not happen to short-circuit within the crystal.

Method of Measuring the Capacity of the Crystals.

Method of Charge and Discharge. — The capacity of the carborundum crystals was measured directly by a method of charge and discharge. A simplified diagram of the circuits employed is shown in Figure 1. By means of a motor-driven commutator C the crystal Cr was con-

[1] G. W. Pierce: "Crystal Rectifiers for Electric Currents," Part I, Physical Review, **25**, pp. 31–60, 1907; Part II, ibid., **28**, pp. 153–187, 1909, and These Proceedings, **44**, pp. 317–349, 1909; Part III, Physical Review, **29**, pp. 478–484, 1909. See also "A Simple Method of Measuring the Intensity of Sound," These Proceedings, **43**, 1908, and "Principles of Wireless Telegraphy," McGraw-Hill, New York, 1910.

nected alternately first with the charge circuit VG′Cr and then with the discharge circuit CrG. A galvanometer, used for measuring the current out of or into the crystal, could be placed either in the discharge circuit at G or in the charge circuit at G′.

When the galvanometer was placed at G and allowed to come to a steady reading, while the commutator C was in operation, the reading

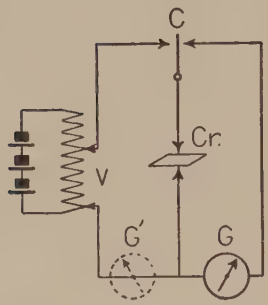

FIGURE 1. Circuit employed in capacity measurements.

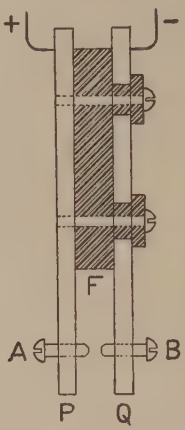

FIGURE 2. Clamp for holding specimen between screws A and B.

of the galvanometer gave the discharge current made up of a series of discharge impulses from the crystal. Placed at G′, the steady deflection of the galvanometer, with the commutator in operation, gave the charge current made up of charge impulses going into the crystal.

The Commutator. — The commutator was made of cold-rolled copper and was used with brushes of the same material so as to avoid thermoelectric currents in this part of the apparatus.

In order to minimize the leak current, the segments of the commutator and the brushes pressing against them were so arranged as to make the time of open circuit between charge and discharge as small as possible.

In order to simplify the interpretation of results, the time of contact for charge was made approximately equal to the time of contact for discharge.

Measurement of Frequency of Commutation. — Various speeds of the commutator were obtained by the use of a series of pulleys of different sizes on the axle of the motor and a corresponding series of different-sized pulleys on the axle of the commutator, which was driven by a

belt from the motor. The speed of the commutator was measured by putting a standard mica condenser in the place of the crystal Cr of Figure 1, and reading the galvanometer at G with a known impressed voltage. In practice, in order to eliminate any errors arising from lack of proportionality of the galvanometer deflections, the impressed voltage was varied so that the readings of the galvanometer in the speed determinations were brought always to the same deflection (20 cm.), under which condition the number of charges or discharges per second was inversely proportional to the voltage required to give the standard deflection.

While the galvanometer deflection and voltage were under observation, one of these speeds was found absolutely by means of a revolution-counter attached to the shaft of the commutator, and the other speeds were then known in terms of the speed given by the revolution counter.

The capacity method of measuring the frequency of charges or discharges had the advantage of permitting instantaneous observations of the constancy of the commutator speed before and after measurements with the crystal as condenser.

Measurements Capable of Repetition. — Although the adjustment of the electrodes upon the crystal so as to get the capacity effects afforded some difficulty, yet when the adjustments were once made, the galvanometer readings, under given conditions, were about as constant with the crystal as capacity as with the standard mica condenser as capacity, and all the observations, with ordinary precautions, were capable of repetition with an error of about 1 per cent, which represented the irregularities of the speed of the commutator.

Galvanometer. — A D'Arsonval Galvanometer of 2000 ohms resistance was used. This galvanometer was provided with a heavy closed-coil electromagnetic damper, so as to obtain steady deflections even with comparatively slow speeds of the commutator. High resistance or high inductance in the galvanometer used with this method of determining capacity, if the capacity is large, is objectionable, because of the danger of having incomplete charge or discharge. In the present experiments attention was given to the matter of the completeness or incompleteness of the charge or discharge. In one of the experiments described below (Experiment II.) the charges and discharges were probably incomplete, but this was due not to the resistance or inductance of the galvanometer, but to the high resistance of the conducting sheets which served, in the crystal, as armatures of the condenser or else to the high resistance of the contacts of the electrodes with these sheets.

Experiment I.

Crystal held in a Clamp. — In this experiment a flat piece of carborundum, about 1 mm. thick, was clamped between two screws A and B of Figure 2. These screws passed through brass supports P and Q insulated from each other by a fibre block F. The screws had copper-plated ends, and were screwed down upon the specimen with sufficient

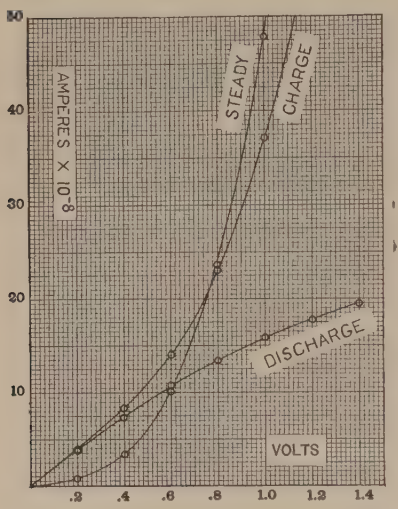

Figure 3. Current *vs.* voltage. A positive. $n = 24.2$.

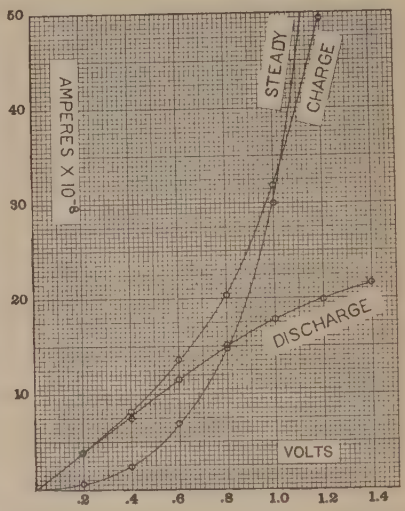

Figure 4. Current *vs.* voltage. B positive. $n = 24.2$.

pressure to cause the brass supporting strips (1 cm. wide and 1.5 mm. thick) to spring apart perceptibly. Later experiments showed that the amount of this pressure probably has no influence on the capacity, so long as the increase or decrease of pressure does not change the position of the contacts with respect to the conducting laminae.

Choice of Specimen. — The particular specimen used in this experiment and the particular setting of the crystal between the supports was obtained only by groping. It had been found accidentally that a specimen of carborundum used in temperature measurements of conductivity showed a slight capacity effect. Incited by this observation, we selected a large number of pieces of carborundum and put them one after the other in the clamp and tested for capacity. Most of them showed no capacity. Finally the piece used in this experiment was tried with the

adjustment that happened to give the capacity effect in a marked degree.[2] Then without changing the adjustment a complete set of data with different speeds and different applied voltages was taken. After the experiment was completed, the specimen was examined with a microscope and was explored electrically while under the microscope, and the existence of the conducting laminae separated by insulating sheets was discovered. After the discovery of these laminae, other specimens could be selected and, with a somewhat difficult adjustment of the electrodes against the conducting laminae, could be shown to act as condensers with larger capacity in some cases than that of the specimens with which the present data were obtained.

Data with Specimen I. — Table I. following contains values of the charge and discharge current obtained with Specimen I, in a circuit of the form of Figure 1, under various impressed voltages and for various numbers of charges and discharges per second. The crystal was connected into the circuit so that one side should be positively charged (see column headed "A positive") and then, without changing the adjustment of the specimen in the clamp, the leads to the crystal were reversed so that it should be charged with the other side positive (see column headed "B positive").

Charge and Discharge Current not a Linear Function of the Voltage. — From these data, sample curves of charge and discharge current plotted as a function of the impressed voltage, with $n = 24.2$, are given, in Figure 3, with the charge applied so that the side A was positive, and in Figure 4 with the charge applied in the opposite direction. Along with the "charge" and "discharge" curves there is plotted, in each figure, a curve of steady current through the crystal obtained when the various voltages were applied directly in circuit with the crystal and galvanometer without the intermediation of the commutator. These curves, which are marked "steady," are the *current-voltage characteristics* of the crystal in the two opposite directions.

The curves of Figures 3 and 4 show that the charge and discharge

[2] In his testimony, on May 22, 1911, in the case of the National Electric Signaling Company *vs.* The United Wireless Telegraph Company, Equity No. 643, District of Maine, Dr. Louis Cohen stated that a certain carborundum detector had a capacity of about .004 microfarads. This result he obtained by measurements with a high frequency generator of 72,500 cycles. So far as we know, his result has not been published except in the Court Record. Dr. Cohen gave no explanation of the phenomenon.

Our own discovery of the capacity was made before the date of Dr. Cohen's experiments, and our delay in publication has been occasioned by a long and tedious search for the explanation of the phenomenon, which we believe we have now found.

TABLE I.

OBSERVATIONS IN MEASUREMENT OF THE CAPACITY OF SPECIMEN I.

No. of Charges or Discharges per Second, n.	Impressed Voltage E in Volts.	Current in Amperes $\times 10^{-8}$.			
		A Positive.		B Positive.	
		Charge.	Discharge.	Charge.	Discharge.
11.43	.2	2.46	2.14	2.35	2.11
for A positive	.4	5.49	4.01	5.20	4.22
and	.6	10.00	5.80	8.87	6.36
	.8	17.90	7.17	15.00	7.85
11.85	1.0		8.23		8.75
for B positive	1.2		9.26		9.50
	1.4		10.22		10.27
16.60	.2	3.17	2.80	3.30	2.71
for A positive	.4	6.80	5.54	6.85	5.60
	.6	11.70	8.05	11.33	8.72
and	.8	20.00	10.02	18.04	11.04
16.90	1.0		11.65		12.79
for B positive	1.2		13.20		14.20
	1.4		14.25		15.55
20.0	.2	3.43	3.20	3.43	3.16
for A positive	.4	7.25	6.34	7.40	6.62
	.6	12.40	9.00	12.13	10.00
and	.8	20.4	11.17	19.30	12.75
20.4	1.0		12.70		14.80
for B positive	1.2		13.98		16.35
	1.4		14.80		17.84
24.3	.2	3.94	3.62	3.94	3.64
for A positive	.4	8.36	7.34	8.21	7.47
	.6	14.00	10.73	13.35	11.50
and	.8	23.05	13.50	20.30	15.04
24.2	1.0		15.83		17.75
for B positive	1.2		17.70		19.80
	1.4		19.50		21.60
29.1	.2	4.41	4.17	4.43	4.25
for A positive	.4	9.21	8.23	9.22	8.71
	.6	15.10	12.10	14.80	13.30
and	.8	23.75	15.32	22.40	17.40
29.5	1.0		17.83		20.32
for B positive	1.2		20.05		22.90
	1.4		21.90		24.40
32.7	.2	5.02	4.43	5.01	4.75
for A positive	.4	10.30	9.25	10.56	9.75
	.6	16.85	13.70	16.77	15.25
and	.8	25.90	17.30	25.02	20.20
33.1	1.0		20.60		23.80
for B positive	1.2		23.20		26.85
	1.4		25.65		29.60
39.80	.2	5.67	5.36	5.78	5.28
for A positive	.4	11.80	10.77	11.96	11.12
	.6	19.10	15.91	19.33	17.16
and	.8	30.35	20.54	28.40	23.03
39.83	1.0		24.75		27.95
for B positive	1.2		28.20		31.95
	1.4		31.45		35.10

current obtained with this specimen is not a linear function of the applied e. m. f. This might have been anticipated from the fact that the leak current through the crystal which increases the charge current

TABLE II.

EQUATIONS OF CURRENT AS FUNCTION OF n.

Impressed Voltage E.	Charge Equation.	Discharge Equation.
	WITH A POSITIVE.	
.2	$I_1 \times 10^8 = 1.3 + 1.12\ n$	$I_2 \times 10^8 = .9 + 1.10\ n$
.4	$3.0 + 2.25\ n$	$1.8 + 2.24\ n$
.6	$6.3 + 3.33\ n$	$1.8 + 3.46\ n$
.8	$13.3 + 4.02\ n$	$1.5 + 4.80\ n$
1.0		$1.5 + 5.85\ n$
1.2		$1.6 + 6.72\ n$
1.4		$1.9 + 7.28\ n$
	WITH B POSITIVE.	
.2	$I_1 \times 10^8 = 1.0 + 1.20\ n$	$I_2 \times 10^8 = .7 + 1.20\ n$
.4	$2.3 + 2.45\ n$	$1.4 + 2.46\ n$
.6	$4.4 + 3.74\ n$	$2.3 + 3.74\ n$
.8	$9.3 + 4.82\ n$	$1.7 + 5.44\ n$
1.0		$1.4 + 6.66\ n$
1.2		$.6 + 7.87\ n$
1.4		$-.1 + 8.35\ n$

and diminishes the discharge current is not a linear function of the voltage.

Charge and Discharge Currents are Linear Functions of n. — If, instead of being plotted against voltage, the charge and discharge current-readings be plotted against the number of charges and discharges per second, the curves of Figures 5, 6, 7, and 8 are obtained. These curves

show that with either orientation of the crystal ("A positive" or "B positive") the current-reading of the galvanometer on charge or on discharge is a linear function of the number of charges or discharges per second.

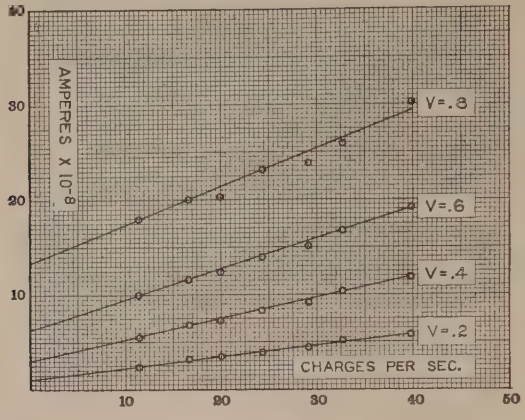

FIGURE 5. A positive. Charge current *vs.* no. charges per second, for various applied voltages *v*.

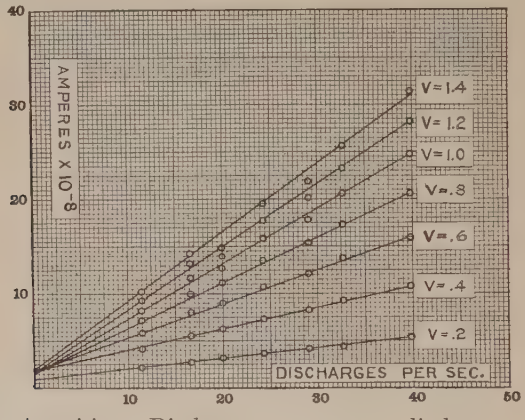

FIGURE 6. A positive. Discharge current *vs.* no. discharges per second, for various applied voltages *v*.

The empirical equations of the curves of Figures 5 to 8, as taken from the curves, are given in Table II. above.

The equations of Table II. agree closely with the data of Table I. The simplicity of these equations indicates that we are dealing with an orderly phenomenon. The linear relation between charge or discharge

current and number of charges or discharges per second, we have taken to indicate that the charge and discharge were practically complete at each commutation; for it is apparent that if this charge or discharge were not complete the incompleteness would be greater at the higher frequencies of commutation and we should not have the linear relation.

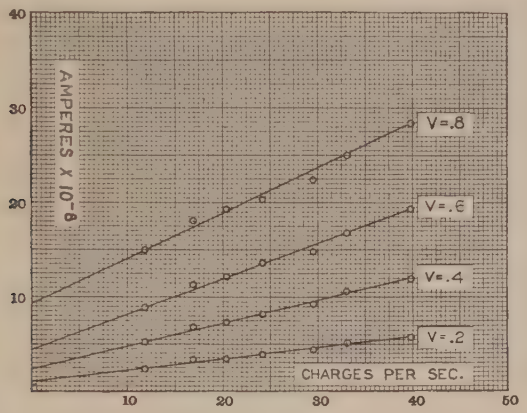

FIGURE 7. B positive. Charge current *vs.* no. charges per second.

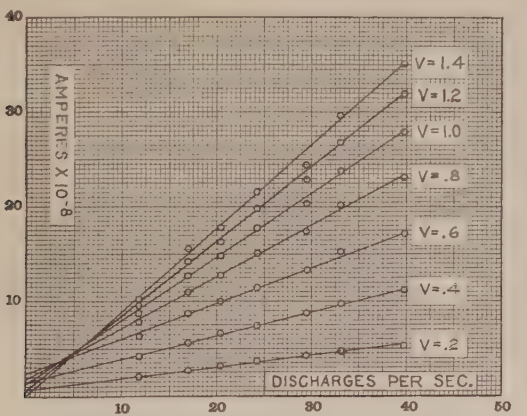

FIGURE 8. B positive. Discharge current *vs.* no. discharges per second.

There follows a mathematical investigation of the phenomenon with the assumption of a complete charge and discharge at each cycle of the commutator. The problem is an interesting one on account of the fact that the leak current through the crystal is not proportional to the voltage.

Theory of Action of Crystal as a Leaky Condenser on the Assumption that Charge and Discharge are Complete.

Let us suppose an e. m. f. E (Figure 9) to be applied to a condenser C through a resistance R, and suppose that the condenser is shunted by a resistance r, through which the leak occurs — the resistance r being of such a character that the current through it is not proportional to the voltage.

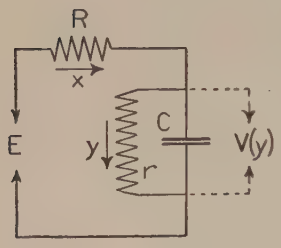

Figure 9.

Let x = the feed current in the main lead R,
y = the leak current through r,
v = difference of potential between the ends of the resistance r; this is a function of y, and is also the p. d. between the plates of the condenser.

These quantities, x, y, and v are functions of the time t.

Kirchhoff's laws give the following equations :

$$E = Rx + v, \tag{1}$$

obtained by taking the e. m. f. around the circuit $ERCr$. ; and

$$\int (x - y)dt = Cv, \tag{2}$$

since $(x - y)$ is the current charging the crystal capacity.

By integration of equation (2) from $t = 0$ to $t = T$, we have

$$q_1 = \int_0^T x dt = C(v_T - v_0) + \int_0^T y dt, \tag{3}$$

in which q_1 is the quantity of electricity flowing through the charge leads during the time T of one complete connection of the condenser to the charging e. m. f.

If we suppose the previous discharge of the condenser to have been complete

$$v_0 = 0. \tag{4}$$

If also we suppose the charge of the condenser is complete in the time T, the current x flowing through the leads at time T is Y, where Y is the steady current through the crystal under the impressed e. m. f. E; therefore, by equation (1), we have

$$v_T = E - RY. \tag{5}$$

Whence equation (3) becomes

$$q_1 = (E - RY)C + \int_0^T y dt. \tag{6}$$

With n charges of the condenser per second, we have for the galvanometer current-reading I_1 in the charge circuit $I_1 = nq_1$; whence

$$I_1 = nC(E - RY) + n\int_0^T y dt. \tag{7}$$

In this equation R is the resistance of the charge circuit from the source of e. m. f. up to the point at which the charge is deposited on the condenser. This includes the resistance of the galvanometer, the resistance of the contacts of the electrodes with the conducting laminae, and the resistance of these laminae up to the point of leak.

Equation (7) is an exact expression for the current-reading of the galvanometer in the charge circuit when the commutator is driven so as not to exceed the speed at which the charge of the condenser at each impulse is complete.

Equation (7), therefore, holds for

$$T \geqq \tau$$

in which T is the time during which the condenser is in charge relation to the circuit during one cycle of the commutator, and τ is the interval required for practically complete charging of the condenser. Let us now break up the last term of equation (7) into two integrals, one from zero to τ and the other from τ to T. During the first of these intervals the leak current $y = y_1$ (say) is variable, and during the second interval the leak current $y = Y$ (say) is constant. Then we have

$$I_1 = nC(E - RY) + n\int_0^\tau y_1 dt + n\int_\tau^T Y dt,$$

in which y_1 is the variable leak current during the short interval for the potential of the condenser to attain substantially its final value, and Y is the steady current through the crystal and the leads under the steady e. m. f. E during the remainder of its connection with the charge circuit. The steady-leak term may be integrated, and we have after integration

$$I_1 = nC(E - RY) + nY(T - \tau) + n\int_0^{\tau} y_1 dt. \qquad (8)$$

Now it should be noted that the quantity nT is independent of the speed, since the geometrical dimensions of the commutator, which is of the rotating type, are fixed. The value of nT is $1/p$, — this quantity $1/p$ being the part of the whole circumference of the commutator occupied by the charge segment. Replacing nT by its value $1/p$, we have

$$I_1 = \frac{Y}{p} + n\{CE - RYC - Y\tau + \int_0^{\tau} y_1 dt\}. \qquad (9)$$

In equation (9) τ is arbitrarily defined as the time for a practically complete charge. Let us be a little more specific and suppose that τ is of such value that when substituted for t in the exponential expression $e^{-\frac{t}{RC}}$ it reduces this exponential to .006. This would make the charge complete so far as measurements of the accuracy of the present experiment would show. If

$$e^{-\frac{\tau}{RC}} = .006,$$

$$\tau = 5RC \text{ (by tables of exponentials).} \qquad (10)$$

With this definition of τ equation (9) becomes

$$I_1 = \frac{Y}{p} + n\{CE - 6RYC + \int_0^{5RC} y_1 dt\}. \qquad (11)$$

This is the equation of current-reading of the galvanometer in the leads to the crystal during *charge*.

Let us next examine briefly the theoretical problem of the *discharge* of the crystal condenser.

A mathematical treatment similar to that of the charge shows that the current-reading of the galvanometer in the discharge circuit, if there are n discharges per second, is

$$I_2 = nCE_0 - n\int_0^{5RC} y_2 dt, \qquad (12)$$

in which y_2 is the leak current during discharge and E_0 is the potential of the condenser at the beginning of the discharge. The potential

of the condenser at the beginning of the discharge is less than E the applied e. m. f. for two reasons; first, because on account of the leak, the crystal was not charged to the applied e. m. f.; and second, because there has been a small loss of charge during the insulation time while the commutator was changing from charge to discharge.

As may be seen by reference to equation (5) the deficiency of potential due to the first of these causes is RY. The fall of potential due to the second of these causes is $\frac{1}{C}\int_0^{T_2} y_3 dt$, in which y_3 is the leak current during insulation, and T_2 is the length of time of the insulation period during each cycle. Therefore the current reading of the galvanometer in the discharge circuit is

$$I_2 = n\{CE - RYC - \int_0^{T_2} y_3 dt - \int_0^{5RC} y_2 dt\}. \tag{13}$$

This is the exact equation on *discharge*.

As an approximation let us suppose that the leak current during insulation was constant and equal to its value at the end of the preceding charge. This is approximately true, because the insulation time was short. With the approximation we have

$$n\int_0^{T_2} y_3 dt = nYT_2 \tag{14}$$

$$= \frac{Y}{m}, \text{ in which } \frac{1}{m} \text{ is the part of the commutator circumference occupied by the insulation segment.}$$

With this approximation equation (13) becomes

$$I_2 = -\frac{Y}{m} + n\{CE - RYC - \int_0^{5RC} y_2 dt\}, \quad \text{(approx.)} \tag{15}$$

in which the first term Y/m is a little too large.

Examination of the Data of Experiment I.

In order to compare the data of Experiment I. with the theoretical equations for charge and discharge current derived above, let us write the charge equation (11) in the form

$$I_1 = \frac{Y}{p} + nEC'_1, \tag{16}$$

in which C'_1 is related to the capacity C by the equation

$$C = \frac{C'_1}{1 - \frac{6RY}{E} + \frac{1}{CE}\int_0^{5RC} y_1 dt}. \tag{17}$$

Likewise writing the discharge equation (15) in the form

$$I_2 = -\frac{Y}{m} + nEC'_2, \tag{18}$$

in which C'_2 is related to the capacity C by the equation

$$C = \frac{C'_2}{1 - \frac{RY}{E} - \frac{1}{CE}\int_0^{5RC} y_2 dt}. \tag{19}$$

Let us now tabulate the values of C'_1 and C'_2 obtained from the experimental data. These quantities which we shall call approximate values of capacity are obtained by dividing the coefficients of n of the equations of Table II. by the corresponding values of E, and are collected in Table III.

In the attempt to get a nearer approximation to the capacity in terms of these coefficients C'_1 and C'_2, it should be noted that the integral terms of equations (17) and (19) are greater than would be obtained by putting y_1 and y_2 respectively equal to zero, and are less than would be obtained by setting y_1 and y_2 equal to their greatest value Y; whence it may be seen from equation (17) and equation (19) respectively that

$$\frac{C'_1}{1 - \frac{6RY}{E}} > C > \frac{C'_1}{1 - \frac{RY}{E}}, \tag{20}$$

and

$$\frac{C'_2}{1 - \frac{6RY}{E}} > C > \frac{C'_2}{1 - \frac{RY}{E}}, \tag{21}$$

in which C is the capacity.

It is, therefore, evident that C, the capacity of the crystal, is greater than the coefficients C'_1 or C'_2 of Table III.

In the attempt to ascertain whether or not the resistance terms could influence the coefficients sufficiently to account for the large

excess of these coefficients with B positive over the corresponding values of A positive, or whether on the other hand it is necessary to assume different capacities in the two opposite directions, we have computed approximate values of the integrals in the denominators of equations (17) and (19). These computations were made by omitting

TABLE III.

Applied Voltage E, Volts.	Approximate Value of Capacity of Specimen I.			
	With A Positive.		With B Positive.	
	C'_1 Farads Charge.	C'_2 Farads Discharge.	C'_1 Farads Charge.	C'_2 Farads Discharge.
.2	$.560 \times 10^{-8}$	$.550 \times 10^{-8}$	$.600 \times 10^{-8}$	$.600 \times 10^{-8}$
.4	.562	.560	.612	.615
.6	.555	.580	.623	.623
.8	.503	.600	.603	.681
1.0		.585		.666
1.2		.560		.656
1.4		.520		.632
average	.545	.565	.619	.639

second-order effects and assuming that the electromotive force on charge is $v_1 = E(1 - e^{-\frac{t}{RC}})$, and on discharge $v_2 = Ee^{-\frac{t}{RC}}$. With these values of the e. m. f. as functions of t/RC and with the steady current-voltage curves of Figures 3 and 4, y_1 and y_2 were plotted as functions of t/RC and integrated by measuring areas, with the result, which is only an approximation, that on charge [3]

$$C'_1 = C\left(1 - \frac{2.6R}{\rho}\right), \tag{22}$$

[3] An independent investigation of the problem imposing the condition that the leak resistance obey *Ohm's law* (i. e. is independent of voltage) leads also exactly to equation (16) for charge and to equation (18) for discharge, with, however, $C'_1 = C'_2 = \frac{C}{\left(1 + \frac{R}{\rho}\right)^2} = C\left(1 - \frac{2R}{\rho}\right)$, approximately.

and on discharge

$$C'_2 = C\left(1 - 1.5\frac{R}{\rho}\right), \tag{23}$$

in which R is the resistance from the impressed e. m. f. into the condenser, and ρ is equal to Y/E and is the resistance to steady e. m. f. of the circuit from the source of e. m. f. through the leads and through the plates and dielectric of the condenser. The resistance ρ is a function of E and is smaller the greater E is.

These equations are consistent with the fact that the coefficient C'_2 on discharge is greater than the coefficient C'_1 on charge. This is seen from Table III. to be true both for A positive and for B positive. Now the current-voltage curves of Figures 3 and 4 show that ρ is smaller for A positive than for B positive. This would make the coefficients for B positive smaller than those for A positive, whereas the converse is the case. In order to explain this discrepancy it is necessary to suppose either

(1) that the capacity of the crystal condenser is actually greater in direction B positive than in the opposite direction, or

(2) that the resistance R is also a function of E and decreases with increasing E more rapidly than ρ does.

The second of these propositions is entirely consistent with previous experiments with carborundum crystals, which showed that if the electrodes were plated to the specimen a large part of the dependence of resistance on current disappeared.

We cannot, however, be sure that the apparent inequality of capacity in the two opposite directions is entirely an effect of leak current ; for we give next data obtained with another specimen with which the leakage through the crystal is almost entirely absent, and yet the capacity given by the measurements is different in the two opposite directions.

Experiment II. Specimen with very Small Leakage.

Mounting in Wood's Metal. — This specimen of carborundum was mounted in a metallic cup in a matrix of Wood's metal. The Wood's metal which served as a solder was placed in the cup and was melted. The specimen was pushed into the molten solder and held with all but its upper face submerged until the solder solidified, forming a close-fitting mold about the specimen. The cup served as one electrode. The other electrode was a pointed brass rod brought down upon the crystal and held by a spring. The cup containing the specimen was

TABLE IV.

Data in Measurement of the Capacity of Specimen II.

No. of Charges or Discharges per Second, n.	Impressed e. m. f. E. in Volts.	Current in Amperes $\times 10^{-7}$.			
		Point Positive.		Point Negative.	
		Charge.	Discharge.	Charge.	Discharge.
11.0	.3			.787	.787
	.6	1.43	1.43	1.66	1.64
	.9	2.07	2.06	2.71	2.54
	1.2	2.68	2.66	4.48	3.52
16.7	.3			1.16	1.16
	.6	2.14	2.14	2.46	2.43
	.9	3.18	3.17	3.98	3.81
	1.2	4.05	4.03	6.20	5.34
22.5	.3			1.59	1.59
	.6	2.92	2.92	3.30	3.27
	.9	4.30	4.29	5.41	5.22
	1.2	5.61	5.59	8.04	7.26
30.9	.3			2.16	2.16
	.6	3.97	3.97	4.42	4.39
	.9	5.92	5.89	7.17	7.02
	1.2	7.64	7.60	10.7	10.0
38.3	.3			2.60	2.60
	.6	4.81	4.78	5.40	5.37
	.9	7.15	7.15	8.72	8.54
	1.2	9.18	9.10	12.75	12.08
46.2	.3				
	.6	5.67	5.67	6.37	6.33
	.9	8.30	8.34	10.17	10.00
	1.2	10.67	10.67	14.76	14.10
54.6	.3			3.48	3.38
	.6	6.41	6.40	7.35	7.34
	.9	9.50	9.50	11.41	11.27
	1.2	12.50	12.30	16.45	15.85

carried by a mechanical microscope stage, so that the specimen could be moved around under the point terminal until a point of contact that gave the capacity effect was located by the capacity measurements. The pressure of the point electrode was then increased so as to avoid accidental disturbance of the connections during the measurements of capacity.

Data. — Current-readings on charge and discharge were taken with the crystal charged so that the point electrode was positive and then with the point electrode negative. Table IV. contains the record.

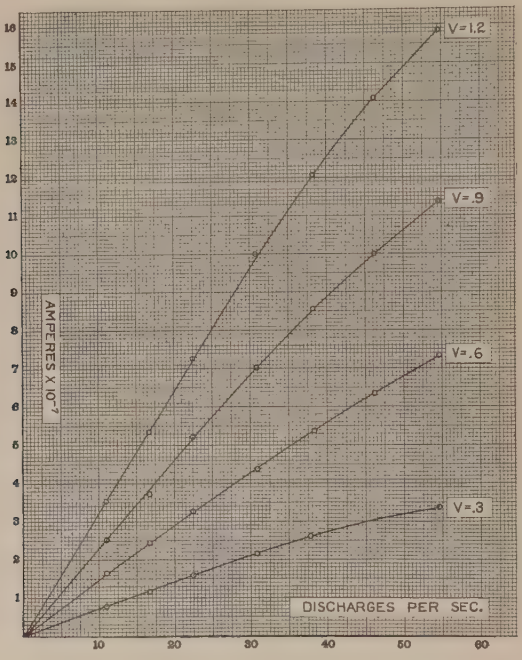

FIGURE 10. Point negative. Discharge current *vs. n*, for various applied voltages *v*.

By a reference to Table IV. it will be seen that with the crystal charged so that the point was positive this specimen gives the same current on discharge as on charge. With this direction of charging *the crystal condenser shows practically no leak.* Table V., which contains the steady current-voltage data for this specimen, shows also that with this direction of application of the e. m. f. the crystal lets through only $.09 \times 10^{-7}$ amperes at 1.2 volts. With the e. m. f. applied in the opposite direction (point negative) the charge and dis-

charge currents (Table IV.) differ by about 5 per cent, at the highest voltage, 1.2 volts. At .9 volts, and lower, this difference is one per cent or less. With the point negative the steady current at 1.2 volts amounts to 1.79×10^{-7} amperes as is seen in Table V. Therefore the crystal with the point charged negative is not non-leaky as with the opposite direction of charging, but the leak is so small as to make the analysis of the problem much more satisfactory than with Specimen I.

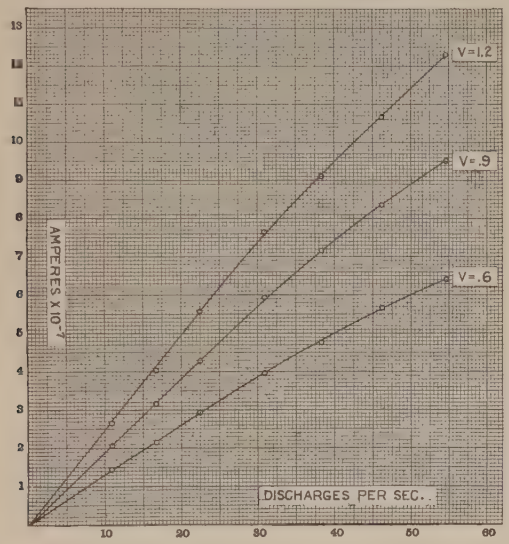

FIGURE 11. Point positive. Discharge current *vs.* n, for various applied voltages v.

Figures 11 and 10 show the discharge current plotted against n, the number of discharges per second, obtained with point positive and point negative respectively. The corresponding charge curves depart so slightly from the discharge curves that they are not here reproduced.

All of the charge and discharge curves for this specimen pass through the origin. This is a result such as one obtains with an ordinary condenser possessing no leakage.

The curves all droop at higher values of n, but are nearly straight for small values of n. Now this fact is in agreement with results obtained with good condensers provided they possess such high resistance in the charge or discharge circuit that the charge and discharge are incomplete. It is interesting that the treatment of the experimental curves of Figures 10 and 11 as due to a condenser with incomplete

charge and discharge leads to the result that the capacity is independent of n but is dependent, as in Experiment I., upon the magnitude and *direction* of the impressed e. m. f. We shall give a brief derivation of the formula for multiple incomplete charge and discharge.

Sketch of Theory of Multiple Incomplete Condenser Discharge.

Let a condenser of capacity C be alternately charged and discharged through a resistance R which is so great as to permit only a partial charge or discharge in the time T of one connection of the condenser into the charge or discharge circuit.

Let the applied e. m. f. on charge be E, and suppose that the charge and discharge have been repeated until a final state is reached.

Let q_1 = quantity of electricity in the condenser at the end of a charge,
q_0 = the quantity in the condenser at the end of a discharge.

If we write down the differential equation for the quantity in the condenser on charge and integrate it subject to the conditions of the problem, we obtain

$$q_1 = q_0 e^{-\frac{T}{RC}} + CE\,(1 - e^{-\frac{T}{RC}}). \tag{24}$$

Similarly from the differential equation for discharge we get

$$q_0 = q_1 e^{-\frac{T}{RC}}. \tag{25}$$

Eliminating between equations (24) and (25) we have

$$q_1 = \frac{CE}{1 + e^{-\frac{T}{RC}}}.$$

$$q_0 = \frac{CEe^{-\frac{T}{RC}}}{1 + e^{-\frac{T}{RC}}}.$$

The quantity of electricity flowing into the condenser during one charge, or out of the condenser during one discharge, is

$$q = q_1 - q_0 = CE\frac{1 - e^{-\frac{T}{RC}}}{1 + e^{-\frac{T}{RC}}}. \tag{26}$$

This equation by expansion becomes

$$q = CE\left(1 - 2e^{-\frac{T}{RC}} + 2\left(e^{-\frac{T}{RC}}\right)^2 - 2\left(e^{-\frac{T}{RC}}\right)^3 + \ldots\right). \quad (27)$$

If we may neglect $2\left(e^{-\frac{T}{RC}}\right)^2$ in comparison with unity, equation (27) becomes

$$q = CE\left(1 - 2e^{-\frac{T}{RC}}\right) \quad \text{approximation.} \quad (28)$$

If there are n charges per second, the current-reading of a galvanometer in the charge or discharge circuit is

$$I = nq,$$

and the time of charge or discharge is

$$T = \frac{1}{pn},$$

where $1/p$ is the fraction of the circumference of the commutator occupied by the charge segment or discharge segment, the two being equal.

With these substitutions equation (28) becomes

$$I = nCE\left(1 - 2e^{-\frac{1}{pnRC}}\right). \quad (29)$$

With the commutator used in these experiments $1/p$ was .48, whence

$$I = nCE\left(1 - 2e^{-\frac{0.48}{nRC}}\right). \quad (30)$$

Examination of the Data of Experiment II.

The curves of discharge current of Figures 10 and 11 with current plotted against number of discharges per second are accurately described by equation (30), as may be seen by reference to Tables VI. and VII., which contain a comparison of observed and calculated values.

The equations of Table VIII. were obtained as follows: Consistent with the theoretical equation (30), the slope of each of the curves of Figures 10 and 11 was taken at the origin. This slope is the coefficient of n in equation (30), and the corresponding coefficient in Table

VIII. Having obtained the slope term, the exponential was next obtained by assuming the upper end point of one of the experimental

TABLE V.

STEADY CURRENT-VOLTAGE CHARACTERISTIC OF SPECIMEN II.

E. m. f. Volts.	Current in 10^{-7} Amperes.	
	Point Positive.	Point Negative.
.3	.004	.012
.6	.02	.083
.9	.04	.45
1.2	.09	1.79
1.5	.165	6.13

curves to satisfy equation (30). This gave the exponent $-165/n$, and by trial the same exponent was found to apply approximately to all of the other curves. That is, all the equations of Table VIII. were ob-

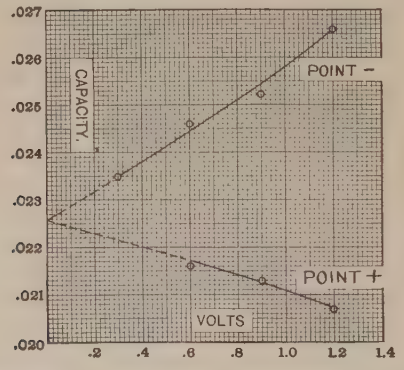

FIGURE 12. Capacity in microfarads of Specimen II. for different values of applied e. m. f.

tained by employing the slope at the origin of each of the experimental curves, and in addition assuming the exponential equation to be correct for one other point of one of the curves. All of the points of all the curves were then found to be closely given by the equations so derived.

The conclusion is that the droop of the several curves of Figures 10 and 11 may be reasonably explained as due to incompleteness of charge and discharge. On this assumption it will be seen that the capacity of the crystal, obtained by dividing the coefficients of the equations of Table VIII. by the corresponding values of E, are functions of the applied

TABLE VI.

DATA OF EXPERIMENT II. COMPARED WITH EQUATION (30).

No. of Discharges per Second, n.	Point Positive. Discharge Current in 10^{-7} Amperes.					
	E = .6.		E = .9.		E = 1.2.	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
11.0	1.43	1.43	2.06	2.11	2.66	2.73
16.7	2.14	2.15	3.17	3.17	4.03	4.09
22.5	2.94	2.94	4.29	4.32	5.59	5.58
30.9	3.97	3.99	5.89	5.90	7.60	7.62
38.3	4.78	4.85	7.15	7.18	9.10	9.26
46.2	6.40	6.42	9.50	9.50	12.30	12.30

e. m. f. and of the direction of charge, while the product of R by C, as given by the exponent, is constant. These quantities are collected in Table IX., and plotted in the curves of Figure 12.

The curves of Figure 12 show that the capacity, as given by equation (30), is changed by a mere reversal of the direction of charge. The capacity is the greater when the point electrode is negative, and with this orientation the capacity increases with increase of applied e. m. f. With the opposite direction of application of e. m. f. the capacity is less and decreases with increasing applied e. m. f.

Whether this result is evidence of a unilateral dielectric constant of the carborundum — which seems improbable — or whether the result is due to an imperfect comprehension of the various factors that may enter into the phenomenon and appear in the final coefficient as capacity, we are at present unable to say.

Among the various factors neglected in the mathematical discussion of the data there is the possibility that heat effects may be important. It looks at first glance as if a thermoelectromotive force at the junction

of the electrode with one of the laminae of the crystal might aid the charge in one direction of charge and hinder it with the opposite direction of charge, and might, hence, cause differences in the capacity coefficients in the two directions, and might also account for the form of the curves of Figure 12. We have submitted the thermoelectric hypothesis to a mathematical treatment, assuming that both Joulean

TABLE VII.

Data of Experiment II. Compared with Equation (30).

No. of Disch. per Sec., n.	Point Negative. Discharge Current in 10^{-7} Amperes.							
	E = .3.		E = .6.		E = .9.		E = 1.2.	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
11.0	.78	.77	1.64	1.59	2.54	2.52	3.52	3.52
16.7	1.16	1.17	2.43	2.42	3.81	3.80	5.34	5.35
22.5	1.59	1.58	3.27	3.26	5.22	5.11	7.26	7.20
30.9	2.16	2.22	4.39	4.58	7.02	7.17	10.00	10.10
38.3	2.60	2.61	5.37	5.38	8.54	8.45	12.08	11.92
46.2			6.33	6.32	10.00	9.95	14.10	14.30
54.6	3.38	3.48	7.34	7.18	11.27	11.25	15.85	15.85

heat and Peltier heat act at the junction of one of the electrodes with the crystal, and have arrived at the result

(1) That the assumption of Joulean heat alone in combination with capacity gives a capacity coefficient that is *the same in the two opposite directions, and for both directions the effect of the heat term is to make the capacity coefficient diminish with increasing applied e. m. f.*

(2) Peltier heat and Joulean heat, if both present in combination with the capacity, would give different capacity coefficients in the two opposite directions, but the effect of the heat would still manifest itself as *an apparent decrease of capacity with increase of applied e. m. f. for both directions of application of the e. m. f.*

Neither of these results is in complete accord with the experimental facts.

Various other possible explanations of the apparent unilateral capacity of the crystal condenser have suggested themselves, but we have

decided to make further measurements before entering into an attempt to consider more of the factors of the problem.

Specimen with Soldered Attachment under Test. — We have succeeded in soldering on the electrodes to one specimen now under test, and are able to preserve the condenser for a more extensive study of its characteristics. Up to the present this study has not added any-

TABLE VIII.

EQUATIONS USED IN CALCULATING VALUES IN TABLES VI. AND VII.

E.	Point Positive. Equation.	Point Negative. Equation.
.3	.....	$I = .0703 \times 10^{-7} \times n(1 - 2e^{-\frac{165}{n}})$
.6	$I = .13 \times 10^{-7} \times n(1 - 2e^{-\frac{165}{n}})$	$I = .144 \times 10^{-7} \times n(1 - 2e^{-\frac{165}{n}})$
.9	$I = .192 \times 10^{-7} \times n(1 - 2e^{-\frac{165}{n}})$	$I = .227 \times 10^{-7} \times n(1 - 2e^{-\frac{165}{n}})$
1.2	$I = .248 \times 10^{-7} \times n(1 - 2e^{-\frac{165}{n}})$	$I = .320 \times 10^{-7} \times n(1 - 2e^{-\frac{165}{n}})$

thing to the results given above. The new condenser leaks badly in one direction but very little in the opposite direction of charge. We are putting it through an ageing process before submitting it to final measurement.

MICROSCOPIC AND ELECTRICAL EXPLORATION OF THE SPECIMENS.

Illumination and Magnification. — Plate I. contains some micrographs of fragments of the crystals. These pictures — which are reproduced with a magnification of 20 diameters — were obtained by reflected light, with the aid of an illuminating objective. The light, which entered the side of the objective, was reflected downward by a prism so that it fell nearly perpendicularly upon the face of the crystal. This vertical illumination from above is most favorable for showing the stratifications in the crystals. Viewed by transmitted light the characteristics are hardly discernible.

Micrograph *a*, Plate I, shows two of the crystallographic angles of the carborundum crystal. The distance between these two vertices is 1.6 mm., and will serve as a convenient standard of reference for the dimensions of the other pictures, which were magnified to the same scale.

Conducting and Insulating Strata. — Micrograph *c* shows very clearly the characteristic stratification, which we have found to be the founda-

tion of the electrostatic capacity of the carborundum. The black lines running in a general horizontal direction across the surface of the specimen are outcroppings of conducting dykes of the crystal; while the white spaces separating the black lines are outcroppings of the insulating matrix in which these dykes are imbedded. The lines which

TABLE IX.

VALUES OF C, RC, AND R FOR SPECIMEN II.

Applied e. m. f. E.	Capacity C, in Micro-farads.	RC in Ohm-farads.	R in Ohms.
FOR POINT POSITIVE			
.6	.0216	.0029	1.34×10^5
.9	.0213	.0029	1.36
1.2	.0207	.0029	1.40
FOR POINT NEGATIVE			
.3	.0234	.0029	1.24×10^5
.6	.0246	.0029	1.18
.9	.0252	.0029	1.14
1.2	.0267	.0029	1.08

are black and white in the pictures are really merely *differently colored* in the crystal. The white regions are generally a transparent blue in the crystals, and the regions reproduced as black are usually seen as brown or red in the specimen.

The difference in electrical conductivity of the dark and light strata was discovered by mounting the specimen in the field of the microscope, and exploring it with two pin-points serving as electrodes. The pin-point electrodes were connected with a battery and galvanometer, or telephone, and were moved about over the surface of the specimen by means of two independent mechanical microscope stages insulated from each other. By means of the slow motion of the mechanical stages, the two pin-points could be put down upon the same dyke or on two different dykes, or one pin could be placed on a dyke while the

other was placed on one of the lighter colored strata separating the dykes.

It was found that the insulation resistance of a very thin layer of the lighter colored material was so great that the current through it under an impressed e. m. f. of 7 volts did not give a perceptible deflection on the galvanometer, that is, the resistance was more than 7000 million ohms, whereas the resistance of the circuit when both pins were upon the same dark-colored dyke was only a few thousand ohms at this voltage.

It was not possible with some of the specimens to get into electrical contact with all of the dark-colored outcroppings, because in some cases it was evident that the outcroppings were in depressions or were coated over so that the electrodes could not be brought against them. With other specimens and with the aid of a telephone receiver in the exploring circuit, we could make attachment of one electrode to a solder-bed in which the crystal was mounted and could draw the other electrode across an exposed face of the crystal in the field of the microscope and hear a click in the telephone as the moving electrode passed over each of the dark-colored outcroppings.

Outcrop of Conducting Points. — In addition to the linear outcroppings of the conducting dykes, there are also with some of the specimens minute points of outcrop of conducting material. Some of these points are visible in Micrograph *d*. They are the globular markings near the left-hand side of the picture. Each globular marking is a minute darker speck surrounded by a whitish circle. In some cases we found an outcrop in the form of a minute speck, which evidently communicated with one or more conducting layers within the crystal, and which showed measurable capacity when one electrode was brought into contact with the speck while the other electrode was in contact with a distant corner of the crystal. In fact, with the specimen of *d* many of the apparently linear outcroppings are made up of discrete points of conducting material.

A Visible Condenser in Micrograph b. — As an illustration of a condenser completely visible, reference is made to Micrograph *b*. The left half of the picture shows two nearly parallel lines running up through the center and down along the left-hand side of the specimen. These lines, which run out of the field at the bottom and top of the picture, were seen, by moving the specimen in the original examination of this specimen, to be really two closed curves, one inside of the other. They are the outcroppings of two practically flat parallel strata nearly perpendicular to the direction of vision. By exploration with the pin-point electrodes these strata were found to be conducting, whereas the whitish

band between the dark lines is the outcrop of an insulating layer separating the two conducting strata. Thus we have a visible condenser in the specimen. The capacity of this condenser was too small to be measured by the method we were employing, and this specimen is kept for future investigation.

Micrograph of Specimen I. — The pictures *e* and *f* of Plate I. show micrographs of the two opposite sides, respectively, of Specimen I. The electrical connection of the specimen into the test circuit was by means of screws set up against the two sides of the crystal. The ends of the screws were so large that the exact point of contact of the screws against the crystal could not be accurately determined, but one of the screw contacts was apparently against the ridge near the center of *e*; the other screw contact was near the center of *f*, which is opposite to *e*. Judging from the large value of the capacity obtained, we are of the opinion that more than one conducting dyke was in contact with each electrode, and that we were dealing with a multiple-plate condenser. Of this, however, we cannot at present be certain, as we have not as yet been able to measure the dielectric constant of the insulating strata, and have not yet been able to determine accurately the geometrical dimensions of the crystal condensers.

Note on Relation of Stratification to Action of Carborundum Crystals as Detectors for Electric Waves.

Not all points of a carborundum crystal are equally good detectors for the electric waves of wireless telegraphy. After our discovery of the existence of alternate conducting and insulating strata in the carborundum crystal, we arranged circuits, with the crystal connected to a multiple-pole switch so that it could be thrown into a wireless telegraph circuit and tested for its sensitiveness to electric waves produced by a test buzzer; then into a circuit of the form of Figure 1, and tested for conductivity and capacity.

The crystal was mounted in the field of a microscope and was carried by a mechanical stage with micrometer adjustment so that different parts of the crystal, while under observation with the microscope, could be brought into contact with the pin-point electrode.

It was found that

1. The crystal and its contact (i. e. the detector) did not respond to electric waves, and did not conduct, and did not have capacity when the point electrode was on one of the light-colored strata;

2. The crystal detector did respond whenever the contact was against one of the darker strata. In general, however, no capacity was dis-

cernible with one of these random adjustments sensitive to electric waves;

3. In rare cases, obtainable only after numerous trials, the adjustment of the contact upon the crystal would give a capacity; in these cases the system would also act as a detector for electric waves.

These observations show that the detection of electric waves occurs for practically any conductive high-resistance contact of the electrode with the crystal, whereas only a rarely attainable adjustment of the contact against a conducting stratum that happens to be pretty well insulated from the other electrode gives the capacity effect measurable by the method of charge and discharge. It is however apparent that if the capacity measurements could be made with the high frequency oscillations of wireless telegraphy, the capacity effect would appear much more commonly.

Summary.

1. An electrostatic capacity is found in carborundum.

2. The capacity-measurements with two specimens are given for different voltage and different frequencies of charge and discharge. The capacity of one of the specimens was about .006 microfarads; that of the other about .022 microfarads.

3. With Specimen I. a leak, different in different directions of charge and not obeying Ohm's law, made the measurements uncertain of accurate interpretation.

4. Specimen II. was practically non-leaky but showed incompleteness of charge and discharge such as would be obtained with a high resistance (120,000 ohms) in the circuit. A reduction of the observation on the assumption of incomplete charge and discharge gives a capacity, which for voltages not zero, is different in the two opposite directions of charge. In one direction of charge the capacity increases with increase of applied voltage; while in the opposite direction of charge the capacity decreases with increase of voltage.

5. The existence of capacity in the crystal was found to be due to the existence of numerous alternate conducting and insulating strata within the crystal. These strata are visible with vertical illumination and moderate magnification.

6. Micrographs showing the stratification are given.

7. So far as the present experiments show, the action of the carborundum as a detector for electric waves and as a rectifier for electric currents is independent of its action as a capacity. But it will detect electric waves or rectify only provided contact is made to one or more of

the conducting strata. It may detect electric waves with an adjustment that shows no capacity by the present method of measuring capacity. On the other hand, with every adjustment at which we found capacity, we found also rectification and detection of electric waves.

Acknowledgment. — The authors gratefully acknowledge their indebtedness to the National Academy for an appropriation from the Bache Fund, which was employed in defraying a part of the expenses of this investigation.

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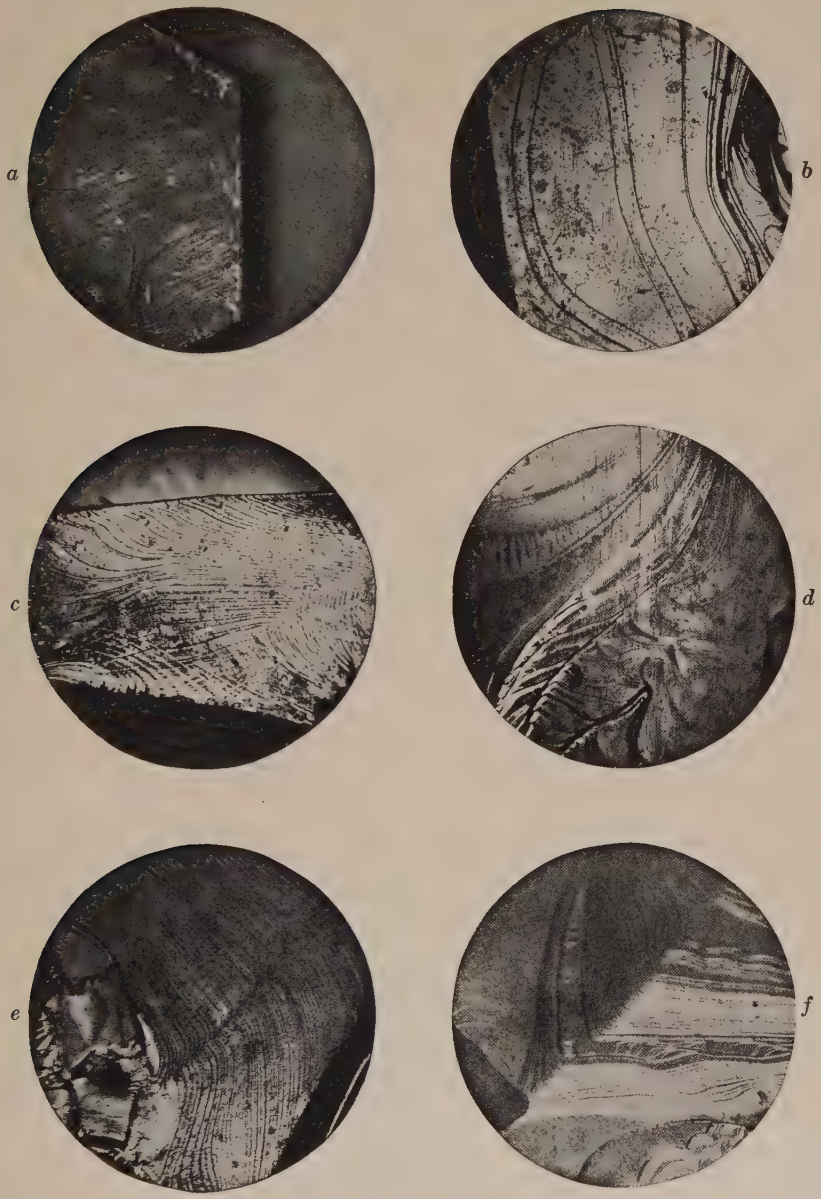
a
b
c
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e
f

Theodore Lyman. Überreicht vom Verfasser.

Die Ionisierung von Gasen durch Licht und das Funkenspektrum des Aluminiums im Gebiete der Schumannstrahlen. (The Ionisation of Gases by Light and the Spark Spectrum of Aluminium in the Schumann Region.)

Von Theodore Lyman.

(Mit Tafel XXIII.)

Die kürzlich im Jahrbuch der Radioaktivität und Elektronik[1]) erschienene Übersicht der Untersuchungen über die Ionisierung von Gasen durch Licht lässt mich vermuten, dass ein paar Bemerkungen über die Spektren von Lichtquellen, die bei diesen Versuchen zur Verwendung gelangen, von Interesse sein dürften.

Auf diesem Gebiete ist die Arbeit von Lenard von der grössten Bedeutung. Da nun Lenard einen sehr kräftigen Funken zwischen Aluminiumelektroden in Luft benutzt hat, wollen wir das Funkenspektrum dieses Metalles im Gebiete der Schumannstrahlen betrachten. Fig. 1 zeigt ein Spektrum, das von einem Aluminiumfunken in einer Wasserstoffatmosphäre erhalten worden ist. Ich habe es hier wiedergegeben, weil es die Struktur des Spektrums zwischen $\lambda = 1600$ Å.-E. und $\lambda = 1870$ Å.-E. veranschaulicht. Einige der Linien, die es aufweist, hat bereits Handke[2]) gemessen. Eine ausführliche Schilderung meiner Arbeiten über dieses Spektrum wird demnächst im Astrophysical Journal erscheinen.

Fig. 2 habe ich von einem Aluminiumfunken in Luft in der Weise gewonnen, dass ich die Elektroden so dicht an das Fenster meines Vakuum-Gitterspektrographen heranbrachte, dass die Entladung über die Oberfläche des Fluorits hinwegstrich. Eine Exposition von sechs Minuten Dauer zerstörte das Fluoritfenster, lieferte aber das Spektrogramm, das in der Fig. 2 wiedergegeben ist.

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1) Jahrb. d. Rad. u. Elektr. **9**, 111, 1912. 2) Inaug.-Diss., Berlin, 1909.

Physikalische Zeitschrift. 13. Jahrgang. 1912. Seite 583–584.

Die Verteilung der Linien, wie sie dieses Spektrum aufweist, liefert eine ausgezeichnete Erklärung der Lenardschen Ergebnisse, wie sie in folgendem Satze zum Ausdruck gebracht worden sind [1]): "Die auf Luft wirksamen Strahlen werden also zum weitaus grössten Teile durch Quarz absorbiert, und zwar ausserordentlich viel stärker durch den Quarz als durch die gleich dicke Luftschicht, welche er ersetzte." Wie ich gezeigt habe [2]), ist eine ein bis zwei Millimeter dicke Quarzplatte bis $\lambda = 1600$ Å.-E. hinunter ganz durchsichtig, aber im Gebiete der Wellenlängen von weniger als $\lambda = 1400$ Å.-E. absolut undurchlässig. Andererseits geht aus meiner Arbeit über die Absorption der Luft [3]) hervor, dass dieses Gas zwischen $\lambda = 1400$ Å.-E. und $\lambda = 1550$ Å.-E. sehr undurchsichtig ist, in der Nähe von 1350 Å.-E. aber seine Durchsichtigkeit wieder anzunehmen beginnt. Berücksichtigt man daher alle diese Punkte, so erscheint es wahrscheinlich, dass die aktiven Strahlen, von denen Lenard spricht, hauptsächlich durch die starke Liniengruppe in der Nähe von 1300 Å.-E. vertreten werden; Licht von dieser Wellenlänge würde nämlich von dem Quarz vollkommen absorbiert werden, könnte aber bei Verwendung einer kräftigen Lichtquelle durch eine Luftschicht von einem Millimeter Stärke hindurch leicht nachgewiesen werden.

Die Energie des Funkens war bei meinem Versuche weit geringer als die von Lenard angewandte. [Mein Umformer braucht im Primärkreise 4 bis 5 Ampere bei 110 Volt, und die Kapazität der Sekundärspule ist 0,025 Mikrofarad.] Indessen glaube ich, dass, wenn nicht eine starke Zunahme der Energie der Strahlungsquelle die Energieverteilung auf die Linien vollständig verändert, das hier gezeigte Spektrum nicht weit von dem Spektrum verschieden ist, das man mit dem Apparat von Lenard erwarten darf.

Fig. 3 zeigt das Spektrum einer Vakuumröhre, die Wasserstoff unter einem Drucke von ungefähr 2 mm enthielt und von einem Umformer aus bedient wurde, der keine Kapazität im Stromkreise enthielt und einen Strom von ungefähr 10 Milliampere verbrauchte. Diese Figur veranschaulicht den grossen Vorteil dieser Lichtquelle vor dem Aluminiumfunken in Luft bei allen Versuchen über Volumen-

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1) Sitzungsber. d. Heidelb. Akad. d. Wiss., Math.-Nat. Kl., 1911, 24. Abh., S. 19.

2) Astrophys. Journ. **25**, Nr. 1.

3) Astrophys. Journ. **27**, Nr. 2.

ionisation. Die Energie ist im Wasserstoffspektrum im wirksamen Gebiet von $\lambda = 1300$ Å.-E. bis $\lambda = 1600$ Å.-E. nahezu gleichförmig verteilt; der Aluminiumfunke dagegen besitzt in diesem Teile des Spektrums nur einige wenige starke Linien. Ein Vergleich der Fig. 2 und 3 zeigt daher sogleich, weshalb Palmer [1]) mit einer Vakuumröhre nahezu ebenso starke Volumenionisation erzielte, wie Lenard mit seinem sehr kräftigen Umformer erhalten hat.

Es dürfte sich empfehlen, vorsichtshalber hinzuzufügen, dass mit Kohlenoxyden gefüllte Vakuumröhren ihrer mangelnden Konstanz wegen für Arbeiten über Ionisation nicht geeignet sind. Eine in geeigneter Weise mit Wasserstoff gefüllte Röhre wird dagegen monatelang konstant bleiben, falls sie nicht überhitzt wird.

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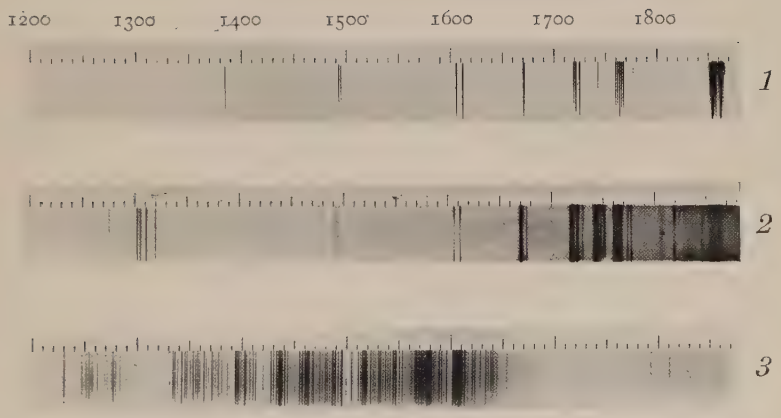
1) Phys. Rev. **32**, 1, 1911.

Jefferson Physical Laboratory, Harvard-Universität, im Mai 1912.

(Nach dem Manuskript aus dem Englischen übersetzt von Max Iklé.)

(Eingegangen 28. Mai 1912.)



h. Lyman, The Ionisation of Gases by Light and the Spark Spectrum of Aluminium in the Schumann Region.

PLATE XVIII

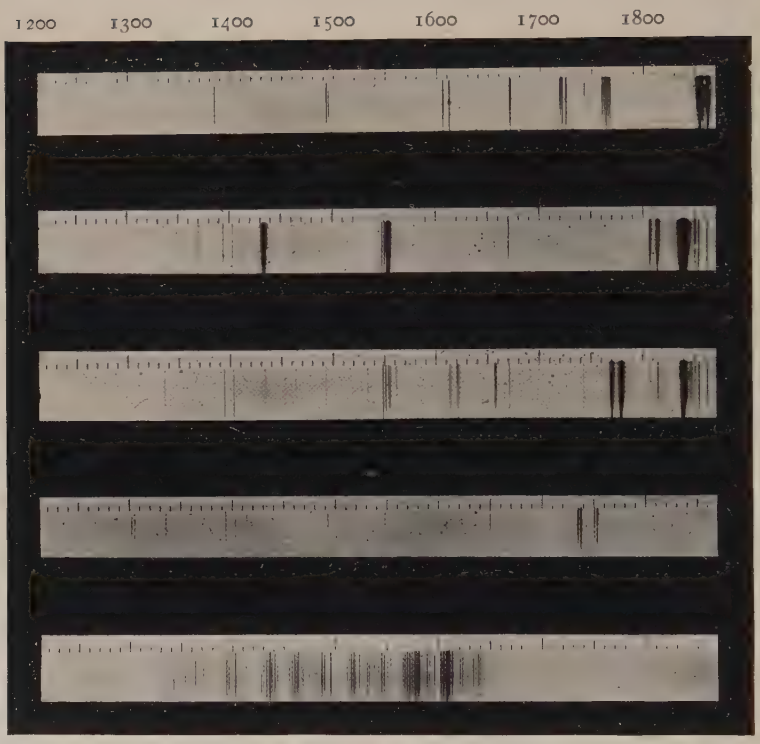


Fig. 1.—Aluminum

Fig. 2.—Calcium

Fig. 3.—Strontium

Fig. 4.—Magnesium

Fig. 5.—Hydrogen vacuum tube

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SPARK SPECTRA OF THE ALKALI EARTHS IN THE SCHUMANN REGION

By THEODORE LYMAN

Spark spectra of metals in the region of extremely short wave-lengths have been investigated by Schumann and later by Handke.[1] The substances studied by the second observer included aluminum, copper, gold, silver, tin, zinc, magnesium, and mercury. The spark was in air outside the instrument. Schumann's vacuum prism spectroscope was used. The measurements extended to the neighborhood of λ 1600. The writer has made experiments on metallic spectra from time to time during the past ten years, using his grating vacuum spectroscope, but without important results until recently, when his attention was directed to the alkali earths by the work of Saunders on series spectra.[2]

The chief improvements which distinguish the present work consist, first, in the employment of a concave grating in place of a prism, and second, in running the spark in a vessel through which a current of hydrogen was maintained. The light thus produced passed directly from the spark chamber through a fluorite window into the body of the spectroscope. In this way, the absorption of the layer of air between the spark and the window was eliminated. At the same time the current of hydrogen helped to free the light-path from the gaseous products of the spark.

Aluminum (Plate XVIII, Fig. 1) was chosen as the first substance for investigation because its spectrum has been studied by Handke and it therefore afforded opportunity for comparing the writer's measurements with measurements obtained by another type of instrument. The figures which will be found in Table I at the end of this paper illustrate in some degree the relative advantages of the two methods of experiment. The greater light-intensity of the prism instrument in the region of wave-lengths less refrangible than λ 1600 is shown by the fact that some faint lines are given by

[1] Inaug. Dis. Berlin, 1909.

[2] *Astrophysical Journal*, **32**, 153, 1910.

Handke which are not easily observed with the grating. On the other hand, the result of the elimination of the absorption of the fluorite prism and lenses and of the air near the spark is illustrated by the fact that the lines of shorter wave-length than λ 1600 were not discovered in the earlier work. Between the two sets of measurements, the agreement is fair; with a few exceptions, the difference between Handke's values and those of the writer are four-tenths of an Ångström unit.

Turning to the principal subject of this paper, the spectra of the alkali earths and their series relations, the expectations in the Schumann region based on theoretical considerations are of two kinds.[1] First, according to the speculations of Ritz and of Saunders there should be series of pairs in the region of very short wave-lengths, the subordinate members of which show constant wave-number separations. Lines belonging to this arrangement have already been observed over the ordinary extent of the spectrum in calcium, strontium, barium, and magnesium, and in the case of some of the series the constants of the formulae have been calculated with a sufficient degree of accuracy to permit of a rough prediction of the position as well as the separation of the new pairs.

The expectation of the second kind is less definite in character than the first. It is founded on the following statement of Saunders:[2] "In all three elements there occurs a strong pair in the ultra-violet: *Ba* λ 2335 and λ 2304; *Sr* λ 2165 and λ 2152; *Ca* λ 1840 and λ 1837, which are reversed in *Sr* and *Ba*, and probably in *Ca* also, and the line of greater wave-length is the stronger in each. They therefore look like subordinate-series pairs in a series of great strength, the rest of which is in the Schumann region."

Confining the attention at present to calcium (Plate XVIII, Fig. 2), the writer's experiments reveal four new pairs, with the separation required by theory, wave-number $1/\lambda = 223$. They appear to fall in with the expectation of the first kind and form terms in the first and second subordinate series. Their discovery is of considerable interest. In the case of the expectation of the second kind, the writer has found three new pairs with the

[1] Ritz, *Physikalische Zeitschrift*, **9**, 521, 1908.

[2] *Astrophysical Journal*, **32**, 165, 1910.

separation predicted by Saunders, $1/\lambda = 70$. These pairs, four in all, may present material for the application of the "combination principle." After lines due to impurities have been eliminated, there remain some ten or twelve lines in calcium unclassified, most of which are faint.

In the case of strontium (Plate XVIII, Fig. 3), the expectation of the first kind is slight. The computations of Saunders show that the limits of the subordinate series lie in the neighborhood of λ 1700; it is a recognized property of these series that the members rapidly decrease in intensity as they near the limit. It is not surprising, therefore, that the writer has observed only one pair with the required separation, $1/\lambda = 800$, in the Schumann region. Their position is λ 1847 and λ 1820. The expectation of the second class, however, has been well fulfilled. There are two striking pairs, with the separation $1/\lambda = 285$.

These three pairs constitute the spectrum of strontium; the other lines visible on the plate are chiefly due to calcium and aluminum.

With barium the experimental difficulties are very great. Success was attained only by using the pure metal in an atmosphere of helium. What has been said of strontium applies even more strongly in this case. The expectation of the first kind is very small. The expectation of the second class is apparently fulfilled: two pairs with the separation predicted by Saunders exist. That they belong together is not absolutely certain, though it seems extremely probable. In addition to these lines, there are several others which may be due to barium.

Finally, the spectrum of magnesium has been studied (Plate XVIII, Fig. 4). It consists, in the Schumann region, of only two pairs, separation $1/\lambda = 90$; they seem to fulfil the expectations of the first class and form members of the first and second subordinate series mentioned by Ritz.[1] The other lines visible on the plate are due to impurities.

In Plate XVIII, the fifth figure shows the vacuum tube spectrum of hydrogen which is added for the sake of comparison. Unfortunately the plate on which the barium spectrum is recorded is not suitable for reproduction.

[1] *Physikalische Zeitschrift*, **9**, 528, 1908.

It is hoped that the results already obtained are of interest in themselves, and it must be remembered that the method may be extended to the study of metallic spectra in general in the region bounded by λ 1850 at the one end and by the absorption of fluorite at the other.

The writer has profited by the advice of Professor Saunders throughout the work. In fact, if it had not been for Professor Saunders' interest in the subject of series spectra in the Schumann region, the research would never have been undertaken.

The details of technique and measurement are to be found in the second part of the paper.

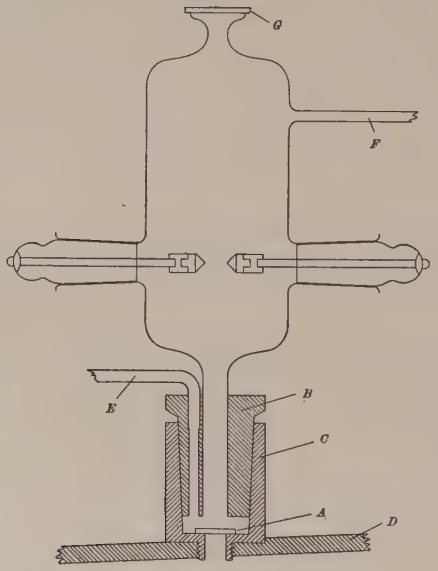

FIG. 1.—The spark chamber

The shape of the spark chamber is illustrated in the accompanying figure (see Fig. 1). A cylindrical glass vessel about 8 cm long and 4 cm in diameter is furnished at one end with a window, and is drawn out into a tube 1 cm in diameter, at the other. This tube fits into a brass cone *B* and is held in place by cement. The cone, in turn, fits air-tight into a cup *C* of the same form as that used in previous work.[1] The cup screws on to the face plate of the vacuum

[1] *Astrophysical Journal*, **32**, 102, 1911.

spectroscope *D* and has attached to it a fluorite window *A*. The point of novelty consists of a tube *E* which penetrates the side of the cone and through which a stream of hydrogen is directed into the spark chamber. This stream of gas, after striking the fluorite window, turns and is directed against the spark discharge and finally makes its way through sulphuric acid into the outer air by means of *F*. By a suitable arrangement of stop-cocks, the spark chamber may be exhausted through *E*. When it was found necessary to replace the stream of hydrogen by an atmosphere of helium, the gas was introduced through the tube *F* after the vessel had been thoroughly exhausted.

In exhausting the spark chamber and the body of the spectroscope itself, the excellent pump made by the Tri-Mount Rotary Power Company of Boston, has recently been employed.

The metal under examination is held in suitable clamps and introduced into the chamber through ground joints as shown in the figure. The discharge is viewed through the window *G* during the course of the experiment. Of late, a Hilger wave-length prism spectrometer has been used for the purpose.

The spark was produced by the Clapp Eastham transformer mentioned elsewhere.[1] In all cases, a capacity of 0.026 microfarads was used in parallel with the coil. In many cases an external spark gap was employed in series with the terminals in the discharge chamber.

It is obvious from what is known of the transparency of gases in the Schumann region that, as the light must pass over a path of more than 6.5 cm between spark and window, the gas in the discharge chamber must be free from impurities, especially oxygen. Hydrogen made from zinc and hydrochloric acid and by electrolysis from a barium hydroxide solution was employed. In both cases the usual precautions as to purification and drying were taken. The gas obtained by the second method gave the better results.

The helium was obtained from Tyrer of London and was used at a pressure of three quarters of an atmosphere. It exhibited a transparency equal if not superior to that of hydrogen. The writer believes that this is the first time the transparency of hydrogen in

[1] *Ibid.*

the Schumann region at atmospheric pressure in a column over 6 cm long has been demonstrated spectroscopically.

The method of measurement was that of shifted spectra, which has already been described in connection with the writer's work.[1] Briefly, it consists in comparing the spectrum under investigation with a known spectrum, generally of iron, which is "shifted" with respect to the first by a given amount. Lately, the process of measurement has been facilitated by the use of a scale specially etched on glass and standardized by comparison with the lines of the hydrogen spectrum. As it was an object to obtain as strong a spectrum as possible, a rather wide slit was used. The definition, therefore, falls short of that obtained in the author's hydrogen plates and in some of his gas spectra work.

The errors are of two kinds: one, which depends on the nature of the method employed, is connected with uncertainties in determining the magnitude of the "shift." This error affects the absolute values of the wave-lengths. With a sharp line in the spectrum of hydrogen it should not exceed 0.2 unit. The other is purely an error of setting and affects the relative values, such as the distance between the pairs. Its magnitude varies naturally with the nature of the line, its minimum is probably about 0.1 unit, its maximum may reach 0.4 in the case of nebulous lines. It is obviously this second error which must be borne in mind in estimating the accuracy of differences in the vibration numbers of the pairs of the same series. It is hardly necessary to add that measurements in the extreme ultra-violet are not well adapted for very accurately determining the constants of the formulae employed in series spectra work.

Impurities in the material employed in the study of spark spectra in the Schumann region may play a double rôle: they may contribute lines to the spectrum and they may form gaseous compounds in the spark chamber which modify the spectrum by their absorption. The metals used were analyzed in the hope that the data thus obtained might afford a clue to the cause of the anomalies observed during the experiment. However, the spectroscope is so delicate a detector of impurities that the results of chemical analysis

[1] *Astrophysical Journal* **23**, 202, 1906.

give only a rough indication of what may be expected. A detailed discussion of the spectra follows.

The specimens of aluminum employed were of commercial quality but of considerable purity. Judging by past experience, they might be supposed to contain only traces of silicon, carbon, and iron. The spectrum in the visible region was dominated by the four lines of hydrogen; the lines of aluminum were relatively feeble. When the spark was tried in helium, the lines of that gas also dominated those of the metal. It is important to notice, however, that in all the spark spectra in the Schumann region, there are no lines which can be traced with certainty either to hydrogen or to helium.

Fig. 1 illustrates the spectrum of aluminum in hydrogen. All the strong lines on the plate are to be ascribed to the metal with the exception of the two pairs at λ 1742.7, 1745.3, and λ 1494.8, λ 1492.8, which are due to a trace of nitrogen.[1] Of the fainter lines, hardly visible in the plate, the one near λ 1655 is probably due to carbon, those near λ 1550 are found in magnesium but may be due to iron, those between λ 1490 and λ 1400 are common to several substances.

Turning to the tables, it is to be noted, that, for most of the lines, the differences between the values obtained by Handke and the measurements of the writer lie between three and four Ångström units. There is an uncertainty in determining the "shift" which introduces the possibility of an error into the writer's values amounting, at most, to two-tenths of an Ångström unit. This error, if it exists, would be of such a sign as to bring the writer's values into closer agreement with those of Handke. However, in the case of the nitrogen pairs at λ 1742.7, λ 1745.3, and in the case of the three lines λ 1721.2, λ 1719.3, and λ 1718.3, the difference in values rises to nearly a whole unit; this fact points to errors of measurements in the work of the earlier observer which may be present in all his data. In the case of the faint lines between λ 1854 and λ 1819, Handke's values alone are given, for although these lines are found on the writer's plate, their rather nebulous character renders their exact measurement difficult.

[1] *Astrophysical Journal*, **33**, 98, 1911.

Very recently the writer has made a new test with the aluminum spark in air. The experiment yielded more interesting results than any of the many previous attempts of this character, its success being due to the fact that the pointed spark terminals were placed nearly in contact with the window of the spectroscope, so that the spark played against the surface of the fluorite. An exposure of six minutes destroyed the fluorite window, but a strong spectrum was registered on the photographic plate. Between λ 1400 and λ 1900 the lines of this spectrum are the same as those observed when the spark was in hydrogen, but there is a distinct difference in the distribution of intensities in the two spectra in this region, owing to the selective nature of the absorption of the air. Near λ 1300, with the spark in air, there is a group of strong lines not observed when the spark was in hydrogen. Of these lines, those at λ 1302.0, λ 1304.8, λ 1305.8, λ 1334.6, and λ 1335.7 are obviously due to some common impurity for they are found with magnesium in hydrogen and with aluminum in helium. The other lines of the group are included in the Aluminum Table but are marked (*) to indicate the uncertainty of their origin.

The specimen of calcium was analyzed with the following result: iron 0.07 per cent, aluminum, magnesium, and silicon, a trace, no trace of barium or strontium or of any other common metal. The spark behaves well in an atmosphere of hydrogen. In Fig. 2 the most striking objects are the strong series of narrow pairs predicted by Saunders. They appear in the illustration as the four broad lines beginning near λ 1370 and ending near λ 1840. On the plate itself, their separation can be measured but their character renders the setting error large, especially in the case of the most refrangible member.

Of the four pairs with wave-number separation $1/\lambda = 223$, predicted by Ritz, only the two at the less refrangible end of the plate are visible in the illustration and of these one member of the first pair is concealed by the strong narrow pair at λ 1840. The other two pairs belonging to this series, though weak, are clearly seen on the original plate. Of the other lines, the sharp narrow pair near λ 1870 may belong to calcium, the lines at λ 1854 and λ 1862 are evidently due to aluminum, the line near λ 1670

belongs to aluminum but seems unduly enhanced here. The nebulous narrow pair at λ 1657 is visible in most metallic spectra both in helium and hydrogen; it is due to a common impurity—silicon or carbon, perhaps. The very faint line near λ 1650 also does not belong to calcium. The background of lines, hardly visible in the illustration, between this point and λ 1555.1 is found in iron, as is also the sharp narrow pair near λ 1550 next to the strong calcium group. The characteristic sharp pair at λ 1393, λ 1402 may be due to calcium but appears in other metals more strongly than their calcium content would seem to warrant. The narrow pair near λ 1335 appear in several metals both in helium and hydrogen. The extreme group not visible in the illustration is found only with calcium; it is made up of some of the most refrangible lines yet obtained with a metal.

Some difficulty was found in obtaining metallic strontium of sufficient purity. A suitable specimen was finally procured, however. It gave the following analysis:

Silicon	None	Calcium	1.5 per cent
Iron	Slight trace	Magnesium	None
Aluminum	Trace	Mercury	None
Barium	None	Carbon	Considerable, not estimated

On inspection of the spectrum, it is obvious that most of the lines are also found in calcium. The only strong lines that can be attributed to strontium are the two pairs at λ 1769, λ 1778, λ 1613, and λ 1620. They also appeared faintly in a spectrum obtained with a less pure specimen of metal.

There is also a weak pair near λ 1821, λ 1847, one member of which may be visible in the illustration, which is predicted by Ritz and Saunders; it has the correct wave-number separation $1/\lambda = 800$.

The magnesium employed yielded the following analysis:

MAGNESIUM

Silicon	None	Barium	None
Iron	0.05 per cent (estimated colorometrically)	Strontium	None
Aluminum	Trace	Calcium	None

On comparing its spectrum with one obtained with iron terminals under similar conditions, it appears that only the two pairs already mentioned can be attributed to magnesium. They appear near λ 1735 and λ 1750. All the other lines are found in the iron spectrum and are due, therefore, either to it or to some impurity common to the two substances. In this connection, it is interesting to observe how small an amount of an impurity may produce an appreciable effect.

The pairs that might be expected at the more refrangible end of the plate cannot be distinguished with certainty from the background of faint lines.

The results of Handke's investigation of the magnesium spectrum do not agree with those of the writer. Perhaps the difference in the condition of the spark in the two cases may account for this.

In the case of barium, the most obvious mode of procedure is to employ carbon terminals saturated with some salt of the metal. An experiment of this kind was therefore tried; carbon terminals saturated with a solution of chloride were used in an atmosphere of hydrogen. The spark showed the barium spectrum in the visible quite strongly, but nothing in the Schumann region.

Through the kindness of Professor T. W. Richards, the writer obtained some unusually pure specimens of barium, containing over 99 per cent of the metal. The impurities were a trace of oxygen and of iron. Experiments with this substance, however, in an atmosphere of hydrogen gave no result at all, perhaps because of the formation of an absorbing cloud of hydride about the spark. Even the results obtained with the spark in helium were somewhat disappointing. The members of the pair λ 1849, λ 1869 have the correct separation $1/\lambda = 575$ and relative intensity, but they are very feeble and rather sharper than one would be led to expect from similar pairs in calcium and strontium. Another pair with correct separation and of a more satisfactory appearance can be picked out from the remaining lines at λ 1678, λ 1694.

The spectrum of hydrogen, which is added for the sake of comparison, was obtained from a vacuum tube in the manner already described.[1] There was no capacity other than that of the leads

[1] *Astrophysical Journal*, **23**, 202, 1906.

in the circuit. The pressure of the gas was about two millimeters. The faint lines on the less refrangible side of λ 1650 are due to a trace of an oxide of carbon.

The similarity between the hydrogen and magnesium spectrum in the neighborhood of λ 1600 is apparent, not real. The two sharp lines, which have been mentioned as occurring most strongly in calcium and whose wave-lengths are λ 1393.6, λ 1402.7, nearly agree in position with the two lines in hydrogen λ 1394, λ 1402.8. It is barely possible, therefore, that these lines are due to the gas, though, as they occur faintly with aluminum in helium, it does not seem probable. If they belong to hydrogen, they are the only lines in the vacuum tube spectrum which appear in the spark.

As usual, the wave-lengths on the table are in vacuum. The scale which is printed with the spectra was not used directly for measurements. It is intended to give the position of the lines only approximately. Of the lines obviously due to impurities the most prominent are given in Table VI.

TABLE I

ALUMINUM

λ	I	1/λ	λ Handke	Diff.	λ	I	1/λ	λ Handke	Diff.
1238.8*...	1	80723	.....	....	1750.0...	3	57143	1750.4	0.4
1264.5*...	1	79083	.....	....	1751.7...	2	57087	1752.1	.4
1275.0*...	3	78431	.....	....	1760.0...	8	56818	1760.4	.4
1276.4*...	2	78345	.....	....	1761.9...	8	56757	1762.4	.5
1310.8*...	6	76290	.....	....	1763.8...	10	56695	1764.2	.4
1319.4*...	6	75792	.....	....	1765.7...	8	56635	1766.0	.3
1326.6*...	1	75380	.....	....	.....	..	.....	1766.9	..
1343.4*...	2	74438	.....	....	1767.6...	8	56574	1768.0	.4
1352.8...	1	73921	.....	....	.....	..	.....	1769.6	..
1379.5...	3	72490	.....	....	.....	..	.....	1772.9	..
1383.9...	5	72259	.....	....	1773.8...	2	56376	1773.8	.0
1540.1...	1	64931	.....	....	.....	..	.....	1774.9	..
1605.6...	8	62282	1605.9	0.3	1776.9...	4	56278	1777.1	.2
1611.8...	8	62042	1612.1	.3	.....	..	.....	1777.8	..
1670.6...	10	59859	1671.0	.4	.....	..	.....	1792.1	...
.....	..	.....	1676.1	..	1818.5...	3	54990	1819.0	.5
1718.3...	1	58197	1719.1	.8	.....	..	.....	1819.6	..
1719.3...	9	58163	1720.0	.7	.....	..	.....	1820.6	..
1721.2...	9	58099	1722.0	.8	.....	..	.....	1833.2	..
1725.0...	10	57971	1725.3	.3	.....	..	.....	1836.8	..
.....	..	.....	1741.1	..	1854.7...	50	.....	1854.7	..
1742.7)	N.	57382	1743.6	.9	1858.2...	10	.....	1858.2	..
1745.3)		57297	1746.3	1.0	1862.8...	50	.....	1862.8	..
1747.7...	1	57218	1748.3	.6					

TABLE II

Calcium

λ	I	1/λ	Δ1/λ	λ	I	1/λ	Δ1/λ
1246.2	1	80244	...	1553.5	7	64370	66
1254.3	2	79726	...	1555.1	8	64304	
1260.2	1	79352	...	1561.2	2?	64053	
1264.5	2	79083	...	1674.1	1	59733	227
1268.2	2	78852	...	1680.5	2	59506	
1276.4	3	78345	...	1692.4	1	59087	226
1369.1	3	73040	80	1698.9	2	58861	
1370.6	3	72960		1807.8	7	55316	220
1393.6	5	71761	...	1815.0	8	55096	
1402.7	4	71291	...	1838.0	9	54406	65
1433.1	5	69778	58	1840.2	10	54341	
1434.3	6	69720		1843.8	6	54236	220
1526.7	2	65501	...	1851.3	7	54016	
1533.4	2	65214	...	1870.4	3	53464	...
1546.0	?	64683	...	1872.5	3	53404	...

TABLE III

Strontium

λ	I	1/λ	Δ1/λ	λ	I	1/λ	Δ1/λ
1532.3?	1	65261	...	1769.8	8	56503	286
1537.9?	1	65024	...	1778.8	9	56217	
1560.8?	1	64070	...	1820.0	1	54945	803
1613.3	4	61985	283	1847.0	3	54142	
1620.7	5	61702					

TABLE IV

Barium

λ	I	1/λ	Δ1/λ	λ	I	1/λ	Δ1/λ
1331.1	2	75126	...	1572.9	2	63577	...
1361.0	2	73475	...	1592.9	1	62778	...
1414.8	3	70681	...	1674.5	4	59719	...
1417.1	2	70567	...	1677.9	3	59598	577
1482.0	1	67476	...	1694.3	6	59021	
1485.0	1	67340	...	1786.6	1	55972	...
1487.0	2	67249	...	1849.5	2	54068	569
1503.9	4	66494	...	1869.2	5	53499	
1554.5	3	64329	...				

TABLE V

Magnesium

λ	I	1/λ	Δ1/λ	λ	I	1/λ	Δ1/λ
1735.0	6	57637	93	1750.9	5	57113	88
1737.8	7	57544		1753.6	6	57025	
				1828.1	1	54702	..

TABLE VI

LINES OF UNCERTAIN ORIGIN

λ	I	1/λ	Δ1/λ	λ	I	1/λ	Δ1/λ
1302.0.....	4	76805	..	1548.2.....	6	64591	..
1304.8.....	3	76640	..	1550.8.....	5	64483	..
1305.8.....	1	76581	..	1649.9.....	3	60609	..
1334.6.....	2	74929	..	1656.8.....	4	60357	..
1335.7.....	3	74867	..	1657.8.....	1	60321	..

In conclusion it may be well to restate the results which have been achieved.

The existence of certain lines in that part of the spectra of the alkali earths which lie in the Schumann region was predicted by Ritz and Saunders on theoretical grounds. When these predictions were made, the spectra of the substances in the region of extremely short wave-lengths had never been observed. The writer has succeeded in photographing these spectra and he has discovered part, at least, of the lines whose existence was predicted. During the work, a method has been developed by which spark and arc spectra may be studied down to the very limit of the transparency of fluorite.

JEFFERSON PHYSICAL LABORATORY
HARVARD UNIVERSITY
May 1912

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Breaking Tests under Hydrostatic Pressure and Conditions of Rupture. *By* P. W. BRIDGMAN.

[Plate II.]

WITHIN the last few years a number of papers* have appeared, either written by engineers or else of engineering interest, dealing with the conditions under which rupture is produced in the materials of ordinary practice. The objects of these papers has been to find if possible some criterion by which rupture may be predicted, whatever the type of applied stress. The present state of opinion seems to be that for ductile materials the maximum shearing stress plays the principal part, but that for brittle materials the maximum principal stress is the determining factor. At the same time it is pretty generally recognized that neither of these criteria is likely to be actually correct, but is at best only an approximation likely to give fairly good results for the materials of ordinary engineering practice under ordinary practical systems of load.

A general consideration of what may be the determining factors in producing rupture under so wide a variation in the nature of the applied stress that there is no immediate relation to the needs of engineering seems to have been neglected. Yet it is precisely such a consideration of the conditions of rupture under as wide a range of the conditions as possible that is likely to lead to a true theory of rupture, and so to a better formulation of the conditions for the range of ordinary practice.

In the course of a number of experiments on very high hydrostatic pressures, the author has observed many cases of rupture which have a bearing on the present question. The pressures which it has been found possible to reach are considerably in excess of any hitherto produced in fluids, pressures of 30,000 atmos. having been repeatedly attained. Under these pressures all ordinary theories as to the behaviour of elastic solids break down completely, and the entire subject had to be approached from the beginning. During the two or three years of preliminary work spent in acquiring familiarity with the methods by which these pressures might

* Scoble, Phil. Mag. xii. pp. 533–547 (1906); Hancock, Phil. Mag. xii. pp. 418–425, 426–430 (1906), and xvi. pp. 720–725 (1908); Gulliver, Proc. Roy. Soc. Edin. xxix. pp. 427–431 (1909); Smith, Eng. lxxxviii. pp. 238–243 (1909); Scoble, Phys. Soc. Lond., Nov. 26, 1909; xxii. pp. 130–146 (1910).

be handled, many cases of rupture have been observed. Several of these appear to be of types not observed before, and they have special bearing on the present question. In this paper three of these types of rupture will be described somewhat in detail, and a discussion given of the bearing of these tests on theories of rupture. No attempt will be made to develop a new theory. All that it is desired to do is to point out that in consequence of these tests the true criterion of rupture must be a much more complicated affair than is ordinarily supposed, and that considerations must be introduced which have been so far neglected, for these tests enable us to summarily dismiss all the conditions of rupture hitherto proposed.

The tests to be described in this paper fall naturally into three types, and the conditions of rupture to which they have application are also three in number, there being one other generally recognized possibility besides the two mentioned in the first paragraph. Each of the three types of tests gives some evidence on the validity of each of the three conditions of rupture, but it will be found that each of the three types of test has its most direct bearing on only one of the conditions. The argument of the paper is grouped about the three different types of test. The nature of the test is first described, then the bearing on the corresponding condition of rupture, and finally the incidental bearing on the other conditions of rupture. The argument is furthermore somewhat complicated by the necessity for keeping in mind the possibility of different criteria holding for brittle and ductile bodies.

The three conditions of rupture to be considered are the condition of maximum principal stress, of maximum stress difference, and of maximum strain. The first demands that rupture occur when either principal stress exceeds a certain value, whether this stress is compressive or tensile. The second demands that failure occur when the greatest shearing stress, or what is the same thing the difference between the greatest and the least principal stress, exceeds a certain value. The third criterion demands that rupture occur if the extension in any direction exceeds a critical value.

Another question of much practical interest, and under ordinary conditions closely related to the question of rupture, is the question as to the conditions under which a material will receive a permanent set. The three criteria just enumerated are very often used interchangeably as either criteria of rupture or as criteria of set.

The first criterion, as originally stated, evidently cannot

hold without modification, for it demands that a solid body when subjected to uniform hydrostatic pressure all over should break when the pressure rises too high. It is inconceivable in this case how the body can break, and the existence of the heavenly bodies with enormous internal pressures is conclusive proof to the contrary. It is still possible, however, that this criterion should be valid as determining set, and that the body might show volume set if the pressure exceeded a certain critical value. This is a question of some interest, and it might possibly seem reasonable at first sight to expect some such set. Kahlbaum * has published results on this subject showing the very surprising result that after the application of pressures up to 10,000 atmos. the density of most metals is increased, due to closing up of small pores, but that beyond 10,000 the density is decreased. Although no systematic investigation of this question has been made in the present work, several incidental determinations have been made up to 25,000 or 30,000 atmos., and no trace of a change of density has ever been found except in those cases where the metal was obviously porous. There seems to be no question but that Kahlbaum's results were due to the fact that he used castor oil to transmit pressure. This freezes under a few thousand atmos., a fact that Kahlbaum overlooked, so that beyond this, his pressure was no longer hydrostatic. This is shown most strikingly by Kahlbaum's own statement that the test cubes were often curiously distorted after application of pressure. Kahlbaum saw in this support of his theory that all metals tend to become plastic or even fluid under high hydrostatic pressures. But it can be stated unqualifiedly from the present work that, on the contrary, substances tend to become more rigid under high pressures. The distortion of the metal cubes found by Kahlbaum is to be explained by the fact that the effect of pressure in increasing rigidity is very different for different substances. It has been found in the present work that under 20,000 atmos. paraffin wax may become more rigid than Bessemer steel.

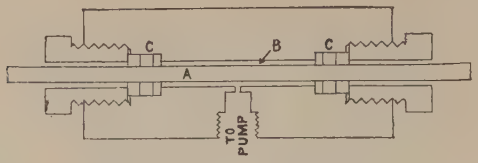
The first criterion is usually modified, therefore, so as to predict rupture when the tension alone, instead of either tension or compression, exceeds anywhere a critical value.

The first type of test has its most direct bearing on the maximum tensile stress criterion of rupture. In these tests cylinders were exposed to pressure over the curved surface

* Kahlbaum, Roth, und Seidler, *Z.S. Anorg. Chem.* pp. 29–30 254–294 (1902).

only, the ends being left unsupported. Fig. 1 illustrates the manner of applying pressure. The rod A, the subject

Fig. 1.



Apparatus for producing the "pinching-off" effect, that is, separation of the longitudinal fibres by the application of pressure to the curved surface of a cylinder. The specimen is shown at A, the fluid exerting the pressure by which rupture is produced is contained in the annular space at B.

of the test, passes completely through the cylinder B, projecting at either end through the packing rings C. The cylinder is connected to the pressure-pump through the indicated connexions and stress applied to the test specimen by the pressure of the fluid in the annular space between the specimen A and the interior wall of the cylinder. The specimen fails by separation of the particles across some plane perpendicular to the axis, the two disconnected ends of the specimen being expelled with violence through the packing rings. The fracture does not take place at the packing rings as might be expected, but, whether for brittle or ductile materials, takes place at some point well between the rings. The nature of the process of rupture is evidently merely that of squeezing the rod out sidewise. This type of rupture may therefore be referred to as the "pinching-off-effect." There is no longitudinal stress except that due to the friction of the packing, and this a stress of compression rather than one of tension, so that here we actually have the fibres separating against the direction of stress.

The nature of the fracture varies with the material. In the case of a rod of mild steel, the rupture looks very much like that of an ordinary tensile break, except that the necking down is likely to be a little more abrupt. Pl. II. fig. 2 shows a photograph of one such specimen. Other soft materials such as copper or brass show the same manner of rupture. Harder materials, such as hardened chrome-nickel steel or vanadium steel, show irregular fracture, a combination of necking down and of slip on shear planes at approximately 45° to the axis. Glass-hard tool-steel, on the other hand, shows a clean break at right angles to the axis without necking down. In the same way it is possible to

break glass rod or heavy glass tubing. The fracture is beautifully clean, exactly at right angles to the axis.

In the cases of the ductile materials, the test is complicated somewhat by the fact that after the necking down has once begun there is a tensile stress tending to pull the bar apart. But this tensile stress cannot account for the beginning of the necking down, so that the tensile stress present during the actual rupture is only an incident due to the particular form of experiment, and is not at all the true cause of the rupture. Evidently there is no such complication in the case of the brittle materials which break with no necking down.

This first type of test disposes of the maximum stress criterion, therefore, as applied to either ductile or brittle materials. It shows *a fortiori*, therefore, that this criterion cannot be applied to brittle materials in contradistinction to ductile materials, as proposed by Scoble *.

Furthermore, the yield or set point and the rupture point practically coincide. No cases have ever been observed of a bar receiving set under this type of stress without rupture. The maximum stress criterion is applicable, then, neither to rupture nor to set.

Incidentally this test disposes also of the maximum stress difference hypothesis, although more direct evidence is afforded by another type of test. The principal stresses for this first type of test consist of a compression equal to the hydrostatic pressure on all planes including the axis, and a small compressive stress due to the friction on the plane normal to the axis. The maximum stress difference is equal to the hydrostatic pressure decreased slightly by the amount of the friction. In the similar case of a bar ruptured by tension, the maximum stress difference is equal to the tension. If the maximum stress difference theory holds, therefore, the "pinching-off-effect" should be produced by a hydrostatic pressure equal to the tensile strength in pounds per square inch. As a matter of fact, the stress to produce rupture always exceeded this by 25 or 50 per cent., except for the glass, when the condition was more nearly fulfilled.

Rupture of the first type has been encountered repeatedly in all this high-pressure work. It is the greatest hindrance to making connexions of any sort from the outside with the interior of a high-pressure cylinder, particularly when connecting one cylinder to another by tubing, or leading electrically insulated electrodes into the interior of the cylinder. Possible rupture of this sort has been the greatest

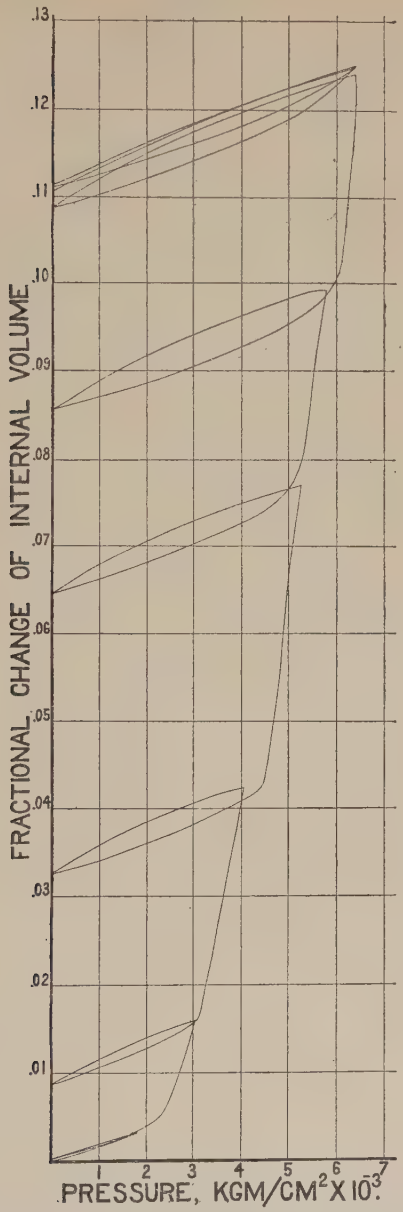
* Scoble, Phil. Mag. xix. pp. 908 916 (1910).

element of danger in this work. On one occasion a specimen 5/16 in. diameter and 3 in. long penetrated 5 inches of wood driven by a pressure of only 6000 atmos. This effect might very probably produce serious consequences for one designing apparatus for the highest pressures without previous experience at lower pressures. The effect is insidious because of the unexpected ways in which it may appear.

The second type of test is very similar to the first in the manner in which stress is applied, but diametrically opposite in its effects. The material for these tests is in the shape of a hollow cylinder, closed at the ends, and subjected to hydrostatic pressure over the entire external surface, on the ends as well as on the curved part of the surface. The tendency of the stress, as is well known, is to collapse the cylinder if the walls are comparatively thin. Such tests are familiar to engineers; the tube folds in on itself in two, three, four, or more creases, depending on the dimensions of the tube originally and on the very slight departure from perfect geometrical symmetry. That there is collapse at all must evidently be due to some slight geometric imperfection. If the tube is made heavier, however, so that geometric irregularities have less effect, the tube does not show collapse by folding under pressure, but shows behaviour of a different sort, depending on the material. Tests of this sort do not seem to have been made hitherto, or at least are not well known, probably because the pressure required to produce the effect is fairly high.

If the material of the cylinder is a ductile metal like mild steel or copper, the effect of the pressure is to close up the hole uniformly, the cylinder retaining its geometric figure. Rupture is never produced in a test of this kind, the hole eventually closing up perfectly tight if the pressure is pushed far enough. This is perhaps as one would expect; the interesting feature of this method of testing is the enormous raising of the elastic limit that it is possible to produce, and the unusual stress-strain relation below the yield point. At one time tests were made simultaneously on seven such hollow steel cylinders. The upper ends of these cylinders were led out of the pressure chamber and connected to graduated glass capillaries. The interior of the cylinders was filled with mercury, so that by observing the rise of mercury in the capillary it was possible to follow the change of internal volume with pressure. No change of length accompanies the closing of the hole, so that the rise of mercury in the capillary gives directly the change of internal volume with pressure. Fig. 3 shows a typical diagram of

Fig. 3.



Shows the relation between internal volume and pressure of a cylinder strained beyond the elastic limit by the application of pressure over the entire external surface.

the test for one cylinder. Pressure was successively applied and removed, each maximum being greater than the preceding maximum. The diagram shows distinctly the location of the yield-point, and shows also that with every application of pressure the new yield-point is not reached until the previous maximum has been passed. This of course is only a verification of common experience as to the possibility of hardening by overstrain. But former experiments on hardening by overstrain have usually been with tensile or compressive or torsion tests, where the possible raising of the yield-point is restricted in amount, a rise of 50 per cent. being large. Here, in these collapsing tests, the possible raising of the yield-point seems to have no limit except that set by the complete closing up of the hole. In the diagram shown above the yield-point has been raised about six-fold; in similar tests with copper, where the complete process has been followed to complete closing of the hole, the yield-point has been raised ten-fold, from 1000 to 10,000 atmos. This was unexpected; one might naturally expect a raising of the yield-point to two or three times the original value, but after this the metal might be expected to flow uniformly towards the centre like any viscous fluid.

The experiments with copper also showed the manner in which the yield-point is connected with flow. The maximum pressure reached in any cycle, plotted against the internal diameter, gave a nearly straight line extending from the original diameter at zero pressure to zero diameter at 10,000 atmos. That is, for equal increments of the yield-point, the diameter decreases by equal amounts. One might expect perhaps that the diameter would tend to decrease more rapidly at the higher pressures. The material of the cylinders after these tests remained perfectly homogeneous, without fault of any kind. Microscopic analysis has failed to reveal anything of interest except a slight elongation of the grains in the direction of flow.

The diagram shows interestingly one other variation in the normal behaviour of metal under high pressure, which is mentioned because of its intrinsic interest, although the bearing on theories of rupture is not so immediate. This is the unusually large hysteresis which goes with the raising of the yield-point. The mere existence of hysteresis as an effect apart from "Elastische Nachwirkung" has even been questioned by some. A diagram like the present shows unmistakably the possibility of this effect entirely apart from any elastic-after-effects. It also suggests that the hysteresis may in some way be connected with an

unstable configuration of the molecules set up in the metal by the overstrain. In the case of ordinary metals, where hysteresis appears before the yield-point of the metal as a whole has been reached, hysteresis is probably connected with local yield in the neighbourhood of the larger or more unstable crystalline complexes of the metal.

The application of all this to theories of rupture is immediate. It suggests, in the first place, that there is no necessary connexion between the yield-point and the rupture-point. Engineers, after some discussion, seem to have accepted the yield-point as the best criterion of rupture. The reason seems to be that the yield-point and the rupture-point are fairly close together, the yield-point is pretty definitely located, and it is possible to calculate the relation between stress and strain up to the yield-point and so to find a criterion at least for yield, if any exists; whereas it is well known that the usual relations between stress and strain break down in the region of viscous flow between the yield- and the rupture-points. Here, in these tests, there is a yield-point but no rupture-point at all, so that certainly, even if a criterion were found for yield, it could not be extended to rupture.

These tests further show that the maximum stress difference criterion of yield is no more valid than the maximum stress difference criterion of rupture. For if the distribution of stress in the cylinder be calculated on the maximum stress difference hypothesis, it will be found that the hole in the cylinder will never close up under any pressure, no matter how large. The mathematical solution of this problem is given in another paper in which this whole question of the collapsing of cylinders is taken up much more in detail*. The solution assumes that the maximum stress difference condition holds throughout the entire extended process of yield. To account for the observed complete closing of the hole it is necessary that the greatest stress difference which the metal can support become less in the last stages of yield. To inquire whether the initial yield always occurs at a definite stress difference would be of little avail, for it is well known, that even for the ordinary tests of engineering the material must first be put into a state of ease by subjecting it to considerable stress. If it is not so subjected to preliminary stress, it may show yield or departure from Hooke's law at values of the stress very much lower than normal. But in tests of this type there is no natural limit to the stress which shall be used to put the

* Phys. Review, xxxiv. pp. 1–24 (1912).

cylinder in a state of ease, and since the diagram shows plainly that the beginning of yield is not sharply defined, there is here no possibility of a natural initial yield-point to which a criterion might be applied.

So far this collapsing test has been discussed only in its application to ductile materials like copper or steel. The behaviour of a brittle material like glass under the same conditions is strikingly different. Cylinders of glass made of heavy capillary tubing sealed at both ends, and hollow spheres with thick walls, have been subjected to hydrostatic pressure up to 24,000 atmos. No permanent measurable change is produced, there being neither crushing nor alteration in the dimensions of measurable amount. It should be said, however, that there must be some slight amount of flow and of interior adjustment to the pressure, although too small to measure, because several of the glass cylinders have broken spontaneously several weeks or even months after the release of pressure. Others have been kept without fracture for a couple of years. One would expect that under the conditions of this test the glass would be crushed. This is the case if the cylinder has not been carefully annealed or if it is geometrically imperfect; the material may then be reduced to an almost impalpable powder. This complete destruction of the minutest fragments of the glass apparently is because the wave of expansion, travelling through the mass after the break has started, at any point is of such intensity that every minute portion is reduced to powder by its own inertia.

For a brittle substance like glass which shows no flow we may calculate the distribution of stress by the ordinary theory of elasticity. It is thus found that the maximum stress difference will occur at the inner surface of the cylinder, and for a thick cylinder will be equal in amount to the external hydrostatic pressure. We have already seen that if the maximum stress difference criterion were valid, the greatest stress difference that the material could support would be equal to its tensile strength. Therefore since the tensile strength of glass is seldom as high as 7000 lbs/in^2, we should have had crushing under the conditions of the test at a hydrostatic pressure no higher than 7000 lbs/in^2, if the maximum stress difference theory were valid for brittle substances. But fifty times this value has been reached without rupture.

The result of this experiment with the glass seems even more unexpected than that with the ductile materials. With the metals we have at least the rearrangement of the

grains produced by the flow as a basis for the raising of the elastic limit, but in a perfectly amorphous substance like glass, which shows no alteration of shape, we have evidence of no such internal change to account for the increase in strength. The experiment suggests a difference between the mechanism of yield and the mechanism of rupture. One can perhaps see why rupture should not occur in the case of the glass cylinders, since there is no place for the fragments to go to in the case of rupture, no way for the rupture to get started. But the same considerations would seem to show also no possibility of yield towards the centre. Yet yield toward the centre does get started and rupture toward the centre does not get started ; there must be some essential difference between the two.

These collapsing experiments also dispose of one other criterion of yield or rupture, better treated by the third type of test. This is the third criterion mentioned above, namely that rupture or yield will occur when the extension in any direction exceeds a critical value. If the strain is calculated in a cylinder exposed to hydrostatic pressure over the outside, the radial strain is found to be an extension at the inner surface. In the case of the ductile materials which flow toward the centre, this radial extension increases enormously with increasing flow, always without rupture or separation of the fibres in the direction of elongation. And in the case of glass under 24,000 atmos, where there is neither rupture nor flow, the elongation at the centre is greatly in excess of the elongation at rupture in an ordinary tensile test, and therefore in excess of the supposed critical elongation.

The third type of test is concerned with the rupture of heavy cylinders by internal pressure. The ordinary theory of the bursting or yield of cylinders under internal pressure is well known. At the inner surface the stress is a pressure on planes at right angles to the radius, and a tension on planes including the axis and radius ; the corresponding strain is a circumferential elongation and a radial compression. At the inner surface the stress difference, the principal stress, the principal strain, and the strain difference all have their maximum values. On any theory of rupture, then, rupture would be expected to start at the inner surface. The precise value of the theoretical bursting pressure depends on the criterion accepted for rupture. If the principal stress criterion is accepted, rupture will occur when the hydrostatic pressure is equal to the tensile strength ; if the maximum elongation is accepted, rupture

will occur for a material like Bessemer steel at an internal pressure about 4/5 of the tensile strength.

The fact is, however, that for the ordinary materials of engineering practice rupture begins at the outside and runs in towards the centre. This rupture may take place either by tearing apart of the metal in an axial plane, or else by slip on a shear plane, the fracture in this latter event running in toward the centre approximately as an equiangular spiral.

Most of these bursting tests were made on drawn bars, which were pierced with the hole first and then turned off slightly on the outside so as to be concentric with the hole. Of course the most obvious suggestion with regard to this rupture from the outside is that there were flaws in the outer skin of the drawn bar penetrating more or less deeply into the interior, and that the rupture started from one of these flaws. In order to prove definitely that this is not the case, the following test was made. A bar of Bessemer steel, $4\frac{1}{2}$ in. diameter, was turned down to 4 in. so as to remove the outer layer. From this 4 in. bar a number of rings, 4 in. in diameter and 1/8 in. square in section, were turned at regular axial intervals of about 1 in. From the bar left after cutting off the rings, a cylinder for testing was made in the usual manner about $3\frac{1}{2}$ in. o. d. and $\frac{1}{2}$ in. i. d. and 8 in. long. From the other end of the same bar a similar set of rings and a similar cylinder were turned, only smaller, the cylinder being 2 in. o. d. and $\frac{1}{2}$ in. i. d. The rings were then tested to rupture on an expanding mandrel. No trace of flaw in the steel was found; the rings expanded between 10 and 15 per cent. before rupture, and the location of the fracture was haphazard, showing no longitudinal vein of special weakness in the steel. The cylinders were then tested to rupture in the usual manner. For this purpose, where the cylinders are made of very ductile material, it was found convenient to fill the cylinders with lead instead of with a true liquid, since it is easier to keep the lead from leaking after the cylinder has begun to stretch. The lead transmits these high pressures nearly hydrostatically. Pressure was produced by a hardened steel piston forced against the lead by the ram of an hydraulic press. A cup-shaped washer of Bessemer steel prevented the lead from leaking past the piston. Because of the very great stretching it was necessary to make several strokes of the piston before rupture was produced.

The results of these two tests with the two cylinders mentioned above are shown in the photographs. The larger

cylinder, Pl. II. fig. 4, broke by separation of the fibres along an axial plane. Break occurred suddenly with explosive report, so that it was not possible to ascertain whether rupture really started from the outside or not. But with the smaller cylinder, figs. 5 and 6, break started more gradually, and it was possible to watch the whole proceeding. In fact, two strokes of the piston were necessary to enlarge the crack to the condition shown in the figure after the first beginnings of the fissure appeared at the outer surface. The fissure appeared first as a small longitudinal crack, which extended itself axially, the central portion gaping wider and wider as the metal on one side protruded by slipping out along a shear plane.

These two experiments showed that the rupture, which apparently begins at the outside, is not produced there by flaws in the steel. There might still be some question as to whether the rupture really did begin at the outside, since of course it is conceivable that the slip had begun at the inside and travelled to the outside, there first becoming noticeable. That the rupture actually does begin at the outside was shown by other experiments on nickel-steel and on copper cylinders. The nickel-steel cylinders do not stretch so much before rupture as the Bessemer cylinders, so that it was possible to produce rupture of these cylinders with a true liquid transmitting pressure. That the rupture really begins at the outside was shown by the appearance of the crack on the outside and its gradual growth, just as above, without any liquid leaking through from the inside, as of course it would have done under the high pressure, 30,000 atmos, if there had been the slightest crack reaching from the centre out. The copper cylinder showed the same thing. Here it was possible by a special arrangement of shrunk-on steel rings to make the necessary connexions and produce rupture with a fluid. Rupture again appeared at the outside first, and spread toward the centre along a shear plane, leak not finally occurring until the crack had opened to the dimensions shown in the photograph, fig. 7 (Pl. II.).

One feature common to all these tests, whether the rupture through the mass of the metal takes the form of a tearing of the fibres or a shear, is that at the inner surface the break is always along a shear plane for a short distance. If the rupture from the outside is by tear, at the inside there are almost invariably two shear planes, running down into the tear. The result is that a sliver of metal in the form of a triangular prism is expelled through the crack. This sliver has been caught on several occasions in a block of lead. It

is difficult to see how this shear along two planes could get started if the crack originally started from the inside. Evidently the crack runs in from the outside until so close to the centre that the prism slips into the crack, driven by the high internal pressure. This universal manner of rupture affords additional evidence, in those cases where the rupture occurs so suddenly that it cannot be observed, that the crack starts from the outside.

The particular bearing of this third type of test on the theories of the conditions of rupture is in showing that the maximum extension criterion does not hold, although of course all the other criteria are also ruled out, if the stress-strain relation is calculated up to the rupture-point by the ordinary theory, because every one of the supposed critical quantities has its maximum value at the inner surface. But the striking feature of all the tests is the enormous stretching of the inner surface without rupture. The Bessemer-steel cylinders of Pl. II. figs. 4 and 5 show a circumferential elongation at the inner surface of 175 and 125 per cent. respectively. The tool steel cylinder of fig. 8 has an interior elongation of 120 per cent. The copper cylinder of fig. 7 shows an interior elongation of 300 per cent. and the lead cylinder of fig. 9 several thousand per cent. There does not seem to be any connexion between the value of the elongation at the exterior surface, where rupture actually does occur, and the elongation under pure tensile tests at rupture. We may have values either greater or less than the tensile elongation. The nickel steel cylinders, those of specially toughened steels, the copper cylinders, and the 3 in. Bessemer cylinder all showed a circumferential elongation at rupture very much less than the elongation at rupture under pure tension. The 2 in. Bessemer cylinder showed an elongation almost exactly equal to that showed by the rings cut from the same piece, while a drawn tube of annealed steel has shown an elongation of 100 per cent. at the outside, and the lead cylinder shows 300 per cent. The tensile value for the steel is about 20 per cent., and for the lead 25 per cent.

Tests on brittle materials like glass also show that the maximum elongation criterion is not fulfilled. Of course, in the case of a brittle material like glass, rupture comes so suddenly and is so complete when it does come that it is impossible to tell by any examination of the fragments whether rupture began at the inside or the outside. But the maximum value of the stress which the glass is capable of standing before rupture is considerably in excess of the theoretical limit. On no theory ought the glass to be able

to stand more pressure on the inside than the tensile test limit, even if the walls of the cylinder are of infinite thickness compared with the bore. One can in cases like this, where there is no yield up to the rupture-point, safely apply the theory of elasticity in calculating the strain up to the rupture-point. This means that no glass capillary ought to be able to stand more than 500 atmos. Capillaries have been found, however, which have successfully withstood 1000 atmos. The question of annealing is of great importance here. Probably with more careful annealing it would be possible to exceed this limit. In any event, the circumferential extension, even when the pressure is only 1000 atmos., must be nearly twice the critical value under rupture in tension.

The manner of rupture described here, beginning at the outside first, is not universal for all materials, but probably holds only for those materials showing considerable plasticity, There can be little doubt but that the rupture of glass cylinders does begin at the inside, and one case in another substance has been actually observed in which the rupture did travel from the centre to the outside. A cylinder of transparent gelatine, about 1 in. o. d. and cast with a concentric hole $\frac{1}{16}$ in. diameter, was ruptured by blowing into it. The rupture took place exactly as the theory predicts ; it started at the inner surface as a tear across an axial plane, and travelled out slowly toward the outside as the interior was more and more distended by blowing.

It is worth while examining these bursting tests a little further, for in this case we can make plausible to ourselves why rupture does not occur at the inside, and so gain an inkling of a much more general criterion than any of those hitherto proposed which must always be satisfied when rupture occurs. If we consider the state of stress at the inside surface we shall find that initially as long as the equations of elasticity hold, the stress consists of a pressure across planes perpendicular to the radius, and a circumferential tension which is greater than the pressure. When the internal pressure becomes too great, however, the inner layers yield plastically, the hole taking a set. During this plastic yield the metal must be thought of as behaving like an imperfect viscous liquid, tending to transmit pressure hydrostatically in every direction. In consequence of the tendency to equality of stress in every direction, the initial circumferential tension becomes a circumferential compression. The mean stress, therefore, at any point of the interior surface becomes a compression after the plastic

yield begins, whereas before yield the mean stress was a tension, because the circumferential tension was greater than the radial compression. The strain, then, after yield, consists of a volume compression at the inner surface, whereas before yield there was a volume extension. Consider now what would happen at the inner surface if rupture were to get started there. We are to think of the general action of rupture as one relieving the stresses at any point, for otherwise the rupture would have no excuse for existence. Before plastic yield, then, rupture at the inner surface would result in release of the volume distension, that is, the volume of the steel would become less. As a result, the compressing liquid would have room to become greater in volume, and the pressure would automatically fall. But if the rupture were to start after the plastic yield, that is after volume compression had taken place at the interior surface, release of the pressure would result only in increase of volume of the steel, the compressing liquid would lose volume, and the pressure would as a result be increased instead of decreased. In this case, rupture, instead of affording relief from the existing state of affairs, would only intensify them. That is, rupture would be an explosive affair, during which work was done against the applied forces instead of by them. This is opposed to all experience. This simply means, then, that even if rupture on a small scale should start at the interior surface during the state of plastic yield, it would be unable to spread. If rupture is to start at the centre and travel out it must start before the stage of plastic yield is reached.

The photograph of the 4 in. Bessemer-steel cylinder, fig. 4, shows this most strikingly. The interior surface is covered with numerous slip bands, some of them very prominent. where the rupture had started but was unable to spread, The pressure on the plastic metal at the inner surface has been so high that a process similar to cold-welding has gone on. The crystalline grains were probably torn apart so as to slip past each other, but the pressure was great enough so that the separation was never beyond the range of molecular attraction, and true rupture did not occur. The copper cylinder also shows the same slip bands at the interior surface.

Another interesting question in this connexion is that of the greatest possible raising of the elastic limit by permanent stretching. It is easy to see that the stress distribution in such a cylinder after the yield-point has been passed and the pressure released is exactly like that in a gun with shrunk-on

hoops. One might expect, then, to be able to reach a pressure abont twice that of the yield-point under pure tension, but as a matter of fact it is possible to exceed this, because of the hardening of the metal by over strain. Thus a copper cylinder, originally $\frac{1}{8}$ in. i. d. and 3 in. o. d. has been subjected to 10,000 atmos. without the yield extending throughout the entire mass. The inner hole has been stretched about 50 per cent. by this pressure. Pressures of 30,000 atmos. have been reached in cylinders of soft nickel steel or of tool steel, and of 40,000 in a cylinder of hardened nickel-steel. But the hardening process by over load is not nearly so complete or thorough as it is for cylinders collapsed by external pressure. The yield under high pressures continues for a very much longer period of time, and the raising of the elastic limit after complete disappearance of set is not permanent. After a period of rest, yield is likely to begin again at a pressure lower than the former maximum. Thus a cylinder of soft nickel-steel, originally 8 in. o. d. and $\frac{5}{8}$ in. i. d., had had the elastic limit apparently raised to 28,000 atmos. by repeated applications of pressure which stretched the inner hole from $\frac{5}{8}$ in. to $1\frac{1}{8}$ in. But now, after several years of use, it is unsafe to subject this same cylinder to more than 15,000 atmos. The initial yield-point of the cylinder was about 8000 atmos.

Summary.

In this paper the results of three types of tests with high hydrostatic pressures have been described in their bearing on theories of rupture. The tests of cylinders under pressure on the curved surface only ("the pinching-off-effect") show that the maximum principal stress criterion is not valid. The tests of hollow cylinders under external pressure show that neither the maximum shear stress nor the maximum shear strain criterion is valid, while the tests on the bursting of heavy cylinders under internal pressure show that the maximum elongation criterion is not valid. These conclusions apply to both brittle and to ductile materials. The tests do suggest that there may be some essential difference between a ductile and a brittle material (more generally between a crystalline and an amorphous one), but show that the distinctions proposed hitherto cannot hold. It is suggested that in every case there must be some more general condition satisfied than those usually considered. There is not enough material at hand to enable a formulation of the condition to be made, but the considerations with regard to the bursting

of cylinders under internal pressure point out what the general nature of the conditions must be. Any entirely general criterion of rupture must demand, among other things, that there be a free space to contain the fragments when rupture occurs, and must also demand that the nature of the rupture be such as to relieve the applied stresses.

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Fig. 2.

Photograph of a "pinched-off" specimen, ruptured in the apparatus of Fig. 1.

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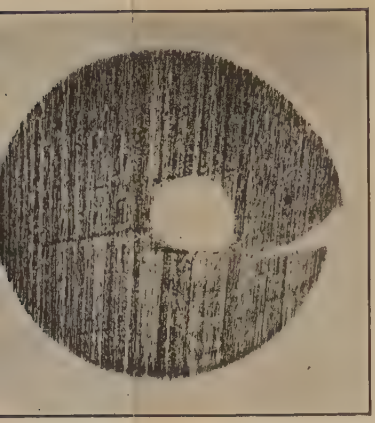
Fig. 4.

One of the halves of a cylinder of Bessemer steel (originally 4 in. in external diameter) ruptured by the application of internal pressure. The

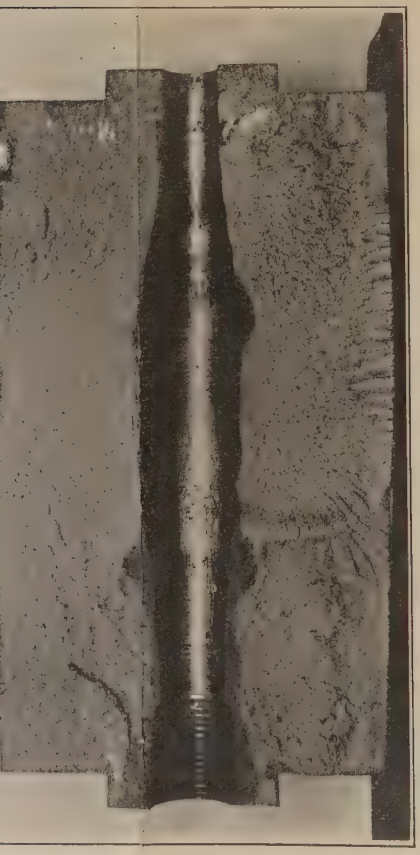
View

Fig. 7.



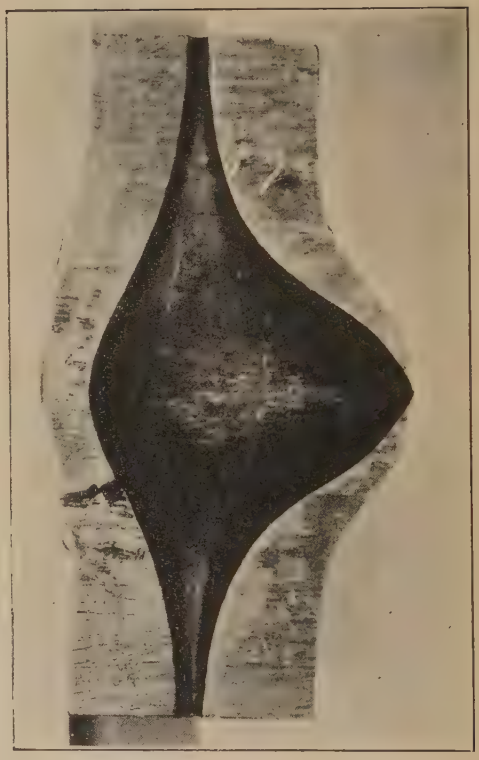
ction of a copper cylinder burst by the cation of internal pressure. The inner hole been stretched from $\frac{1}{8}$ in. to $\frac{3}{8}$ in.

Fig. 8.



e halves of a cylinder of tool steel split by the cation of internal pressure. The inner hole tretched from $\frac{1}{8}$ in. to $1\frac{1}{2}$ in. The maximum

Fig. 9.



Longitudinal section of a cylinder of lead burst by the application of internal pressure. The elongation at the outside at the locality of rupture is over 300 per cent.

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THE IMPEDANCE OF TELEPHONE RECEIVERS AS AFFECTED BY THE MOTION OF THEIR DIAPHRAGMS.

By A. E. Kennelly and G. W. Pierce.

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I. Introduction.

The writers have made a series of measurements of the resistance and inductance of several forms of telephone receivers over a wide range of frequency of current. In the course of the measurements some interesting results have been obtained, which form the subject of this paper.

As the period of the e. m. f. used in the measurements approaches the natural period of the diaphragm, the note emitted by the telephone receiver increases markedly in loudness, and the resistance and inductance of the receiver undergo wide deviations from values obtained when the diaphragm is prevented from vibrating by being damped. That is to say, the motion of the diaphragm has an effect upon the resistance and inductance of the receiver, and this effect grows rapidly as the electrical period approaches the mechanical period.

In the tests to be described, the resistance and the inductance of a given receiver were measured, first with the diaphragm free and sounding, and, second, with the diaphragm damped, or arrested. The values when the diaphragm is free may be called *free values;* the values when the diaphragm is damped may be called *damped values.* The difference obtained by subtracting the damped values from the corresponding free values may be called the *motional values* of resistance, inductance, etc.; since such differences are due to the motion of the diaphragm.

It is found that when the impressed frequency differs widely from the natural frequency of the diaphragm, the motional resistance and inductance are very small. In the neighborhood of resonance, which is often very sharply marked, these motional values become relatively large, and one or both pass through a change of sign, in such a manner that, when the motional impedance for different frequencies is drawn vectorially from a fixed point as origin, all the points given by the observations lie upon a circular graph, which may be called the *mo-*

tional impedance circle, or for brevity, the *circular graph* of the receiver. Different telephone receivers have very different circular graphs, and the circular graph of any given receiver defines its characteristics in various important practical respects, both mechanical and electrical.

Also, from a theoretical standpoint, the reactive influence of the motion of the diaphragm upon the current through the coils of a tele-

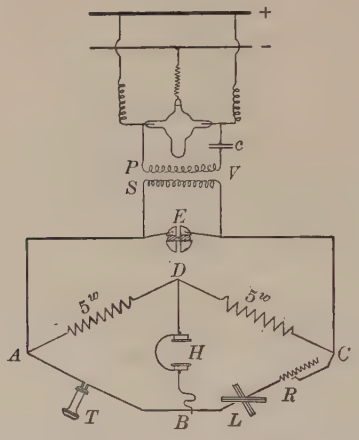

FIGURE 1. Diagram of connections of the Rayleigh Bridge and Vreeland Oscillator.

phone is interesting from its analogy to the effects of an optical medium upon transmitted light in the neighborhood of an absorption band.

The experiments also give information regarding the natural period of vibration, and the natural damping factor of the diaphragm, and the power drawn by the instrument when it is sounding and when it is damped.

II. METHOD AND APPARATUS.

Measurement of Resistance and Inductance.— The measurements of resistance and inductance were all made with a Rayleigh equal-arm bridge, with connections as indicated in Figure 1. The arms AD and DC of the Bridge were 5-ohm non-inductive resistances. The Arm AB contained the telephone receiver T under test. The arm BC contained the adjustable non-inductive resistance R and the adjustable Ayrton-Perry Variometer L. A head telephone H served to determine a balance.

The source of e. m. f. used in the measurement was a Vreeland Sine-Wave Oscillator [1] V, capable of supplying any desired frequency between the limits 430 and 2400 cycles per second. The secondary coil S of the Vreeland oscillator was connected to the bridge terminals *A* and *C* through a resistance of usually 50 or 100 ohms, not indicated. The potential difference of the Vreeland secondary terminals was kept constant throughout a given set of measurements, and was measured by a Paul static voltmeter E. In order to approximate working conditions in the telephone, the voltage at E was kept down to a low value (6 to 12 volts, differing in different experiments). From the known voltage at E, the voltage at the terminals of the telephone was known, and was maintained in different series of tests at values between 0.3 and 1.0 volt.

Measurement of Frequency.— The frequency of the oscillator was measured by comparing the pitch of the sound from the telephone *T* with that of a set of 75 tonometer tuning forks, ranging from 256 to 552 vibrations per second, with successive differences of 4 vibrations per second. Intermediate pitches were estimated by beats. As a check, a stroboscope was in some instances used upon the flickering illumination from the Vreeland bulb, but this was found to be much less convenient than measurement by the tonometer. The pitches were also obtained by calculation from the electrical constants of the Vreeland oscillation circuit, and this method was found to be the most reliable in interpolations for small changes of frequency. In order to obtain the small gradations of frequency that were sometimes necessary, an auxiliary standard condenser was used in connection with the condensers in the Vreeland oscillation circuit. In certain cases it was necessary to vary the capacity in successive measurements by increments as small as 0.001 microfarad.

Procedure.— The procedure in making a test was as follows: The frequency of the Vreeland oscillator was first set to the required value by the adjustment of the capacity, and occasionally of the inductance, of its oscillation circuit. The magnitude of the voltage at the Vreeland terminals was then adjusted by adjusting the distance between the primary and secondary Vreeland coils, while an observer watched the indications of the Paul static voltmeter *E*. A balance on the Rayleigh Bridge was then obtained by successive adjustments of *R* and *L* (Figure 1) with the diaphragm of the telephone *T* free and sounding. After recording the values of *R* and *L* so obtained, the balance

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1 Physical Review, **27**, p. 286, 1908.

was repeated with the diaphragm of the telephone T at rest and silent. The damping was effected usually by lightly pressing upon the diaphragm with the finger, but in some cases it was affected by inserting a light wedge (a quill) between the diaphragm and pole, when this operation was permitted by an open structure telephone. The balance, when the diaphragm was damped, gave practically complete silence in the head-telephones H, and the settings of resistance and inductance were consistent within about $\frac{1}{2}$ of 1%. The balance, on the other hand, when the diaphragm was in motion, was not so good. In this case, difficulties were introduced by parasitic notes probably due to currents of higher frequency generated by the motion of the telephone diaphragm. It was usually possible, however, to balance out the fundamental tone, with adjustments consistent within 1 or 2 ohms.

III. Particulars of the Telephones Tested.

Several telephones were submitted to measurements. Four of the instruments, for which the results are presented in the present account, were:—

1. A Western Electric Bipolar Bell Telephone, Type 122, here designated "R_b",
2. A Western Electric Bipolar Watch-case Telephone receiver, designated "Watch-case,"
3. An experimental specially-constructed monopolar receiver, here designated "Experimental monopolar," and
4. An experimental bipolar telephone receiver, provided with exploring coils, and here designated "Experimental bipolar."

The following table (Table I) contains some of the mechanical particulars of these instruments.

IV. Experimental Data and Results.

The data obtained by measurements of the resistance and inductance of the first three of the above receivers are contained in Tables II to VI. The data with the "experimental bipolar" receiver are not tabulated, as they were taken for the specific purpose of determining the angle of lag of magnetization of the iron behind the actuating current and this subject is discussed later.

Explanation of Tables.— A brief explanation of Table II, obtained with the bipolar Bell "R_b" with 0.3 effective volts applied at its terminals, will be given as typical of all the tables. The first column

contains the frequency in cycles per second. The second column gives the corresponding angular velocity in radians per second. The third column gives R′ the resistance free, at each frequency, as measured on the Rayleigh bridge; while the fourth column gives R the corresponding resistance obtained with the diaphragm damped. The

TABLE I.

MECHANICAL CONSTANTS OF RECEIVERS.

	Bell R_δ.	Watch-case.	Exp. Monopolar.	Exp. Bipolar.
Area of each pole in cm. × cm.	1.4 × .225	1.61 × .16	0.53* × 0.53	1.17* × 0.38
Distance separating poles in cm.	0.85	0.80	—	0.73
External diam. of diaphragm in cm.	5.40	5.48	7.22	7.22
Diameter of clamping circle, cm.	4.94	4.84	4.45	4.45
Tchikness of diaphragm, cm.	0.024	0.030	0.032	0.022
Weight of diaphragm, grams	4.0	5.03	5.3	5.3
Direct-current resistance of coils, ohms, at 20° C.	71.0	81.4	89.7	25

* Laminated poles.

fifth column, headed "motional," gives R′ — R; or the difference between the free and damped resistances with a proper sign for the difference. The three remaining columns contain the corresponding reactances, as obtained by multiplying the inductances observed on the Rayleigh bridge by the angular velocity ω in each case. The final column, marked "motional," gives the excess of free reactance over damped reactance, with proper sign.

Tables III to VI contain data similar to those in Table II, but with different applied voltages or different receivers.

An examination of these tables shows that there are two independent phenomena of interest; namely;

First, the effect of the frequency on the resistance, reactance and inductance of the receiver when damped; and

TABLE II.

RESISTANCE AND REACTANCE OF BIPOLAR BELL RECEIVER R_b, AT DIFFERENT FREQUENCIES.

0.3 VOLT AT TERMINALS.

Frequency.		Resistance, Ohms.			Reactance, Ohms.		
n. Cycles per Second.	$\omega = 2\pi n$ Radians per Second.	Free R'.	Damped R.	Motional $R' - R$.	Free $X' = L'\omega$.	Damped $X = L\omega$.	Motional $L'\omega - L\omega$.
440	2760	151.8	146.3	5.5	138.1	135.1	3.0
512	3220	163	150.8	12.2	148.7	144.5	4.2
600	3770	166	147.7	18.3	154.5	150.5	4.0
670	4210	188	157.5	30.5	162.4	158.8	3.6
704	4420	206	163.0	43.0	162.0	164.2	− 2.2
720	4520	213	164	49	158	166	− 8.0
744	4660	233	168	65	142	168.8	−26.8
754	4730	237	170	67	133.2	169.5	−36.3
770	4830	240	172	68	115.7	172.3	−56.6
778	4880	212	173	39	78.1	171.4	−93.3
780	4900	173.5	173	0.5	76.5	170.5	−94.0
790	4960	164	172.5	− 8.5	82.3	173.0	−90.7
792	4970	164	172.5	− 8.5	81.9	173.2	−91.3
792	4970	172.5	183	−10.5	78.4	165.9	−87.5
792	4970	178	175	3	78.4	173.6	−95.2
793	4975	169	175	− 6	78.5	172.9	−94.4
794	4980	178	172.5	5.5	75.6	173.5	−97.9
804	5050	142	178.5	−36.5	122	174	−52.0
808	5080	148	177	−29	98.4	174.9	−76.5
822	5160	146.5	180	−33.5	145	175	−30.0
824	5180	142	180	−38	121.6	180.0	−58.4
824	5180	136	176	−40	120.4	177.2	−56.8
826	5190	141	176	−35	117.7	177.9	−60.2
826	5190	141	176	−35	127.2	177.9	−50.7
832	5220	147	179	−32	145.7	172.9	−27.2
840	5280	157	182	−25	162.8	177.5	−14.7
868	5450	160	183	−23	167	181	−14.0
890	5590	166	186	−20	175	184	− 9.0
892	5600	164.5	185	−20.5	175	184	− 9.0
912	5730	180	204	−24	184	192.5	− 8.5
940	5900	178.7	191.5	−12.8	183.5	187.8	− 4.3
1000	6283	205	203	− 8.0	202.5	204	− 1.5
1060	6650	210	216	− 6.0	209.5	211.5	− 2.0
1152	7250	192	202	−10	230.5	234	− 3.5
1248	7850	222	225	− 3	230	228	2.0
1648	10350	264	265	− 1	254	253	1.0
2464	15500	325	325	0.0	291.5	294	− 2.5

Second, the effect of the motion of the diaphragm. These two effects will be treated in order.

Change of Damped Resistance, Inductance and Reactance with Change of Frequency.— Figure 2 shows the damped resistance, inductance and reactance of the bipolar receiver "R_b" plotted

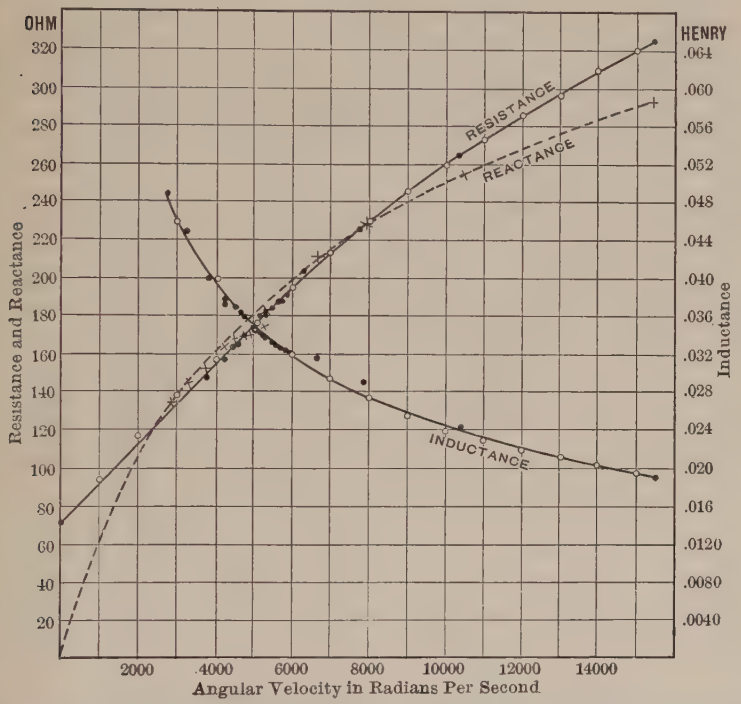

FIGURE 2. Curves of damped resistance, inductance, and reactance plotted against angular velocity, for Bell bipolar receiver, with 0.3 volt at terminals. The dots are observed points; circles calculated; crosses belong to reactance curve.

against the angular velocity of the current used in the measurements. Figure 3 contains the corresponding curves for the bipolar "watch-case" receiver. In each case the resistance and reactance of the telephone when damped increases with increase of frequency, while the damped inductance decreases with increase of frequency. The following empirical relations approximately hold.

For the bipolar Bell "R_b," at 20° C, and with 0.3 volts at its termi-

TABLE III.

RESISTANCE AND REACTANCE OF BELL BIPOLAR RECEIVER R_δ AT DIFFERENT FREQUENCIES.

0.42 VOLTS AT TERMINALS OF RECEIVER.

Frequency.		Resistance, Ohms.			Reactance, Ohms.		
n. Cycles per Second,	ω Radians per Second.	Free R'.	Damped R.	Motional $R'-R$.	Free $L'\omega$.	Damped $L\omega$.	Motional $L'\omega - L\omega$.
428	2690	138	128.5	9.5	129.5	124.4	5.1
548	3446	162	145.7	16.3	148.8	144.3	4.5
704	4425	211	168	43	164.2	166.4	− 2.2
710	4468	216.5	167.5	49	160.7	166.9	− 6.2
722	4540	224	172	52	155.1	168.7	− 13.6
733	4610	230	170	60	148.7	170.4	− 21.7
744	4680	235	171.5	63.5	144.1	170.4	− 26.3
754	4740	242.5	175	67.5	132.1	171.4	− 39.3
766	4810	237	174	63	120.5	171.6	− 51.1
778	4885	227	175	52	90.8	172.9	− 82.1
792	4976	189	176	13	76.1	177.1	−101.0
805	5060	154	177	−23	94.1	177.5	− 83.4
822	5170	142	181	−39	127.8	179.5	− 51.7
836	5253	143	181	−38	142.9	179.7	− 36.8
853	5354	148	183	−35	156.3	183.1	− 26.8
870	5470	157	185	−28	167.9	184.3	− 16.4
890	5595	161	186	−25	171.5	187.2	− 15.7
2464	15480	306.5	306.5	0.0	291.9	296.5	− 4.6

nals, the damped resistance as a function of the angular velocity is expressible by the equation

$$R = 71 + 0.0234\,\omega - 0.456 \times 10^{-6}\omega^2 \qquad \text{ohms,} \quad (1)$$

in which R is the damped resistance, and ω is the angular velocity in radians per second.

TABLE IV.

Resistance and Reactance of Watch-case Receiver, at Different Frequencies, with 0.3 Volt at Terminals of Receiver.

Frequency.		Resistance, Ohms.			Reactance, Ohms.		
n. Cycles per Second.	ω Radians per Second.	Free R'.	Damped R.	Motional $R'-R$.	Free X'.	Damped X.	Motional $X'-X$.
451	2834	135	136	− 1	115.7	118.5	− 2.8
550	3456	149	149	0	135.8	135.8	0.0
653	4102	163	160	3	150.3	149.5	0.8
702	4410	168	166	2	162.6	160.8	1.8
712	4474	174	171	3	157.4	157.0	0.4
753.5	4738	179	175	4	163.5	163.0	0.5
804	5052	185	181	4	169.5	168.0	1.5
849.5	5340	194	184	10	172.5	174.7	− 2.2
884.3	5554	204	187	17	171.2	178.4	− 7.2
903	5674	212	189	23	160	180.5	−20.5
913	5736	207	190	17	146.1	180.5	−34.4
923	5800	192	191	1	137.8	182.5	−44.7
934	5868	174	192	−18	146	183.5	−37.5
940	5906	169	193	−24	154.4	184.5	−30.1
945	5938	168	193	−25	160.1	184.5	−24.4
957	6014	170	194	−24	172.2	186.0	−13.8
968	6082	173	195	−22	177.6	186.8	− 9.2
980	6158	179	197	−18	182.8	186.5	− 3.7
993	6240	183	198	−15	186.6	188.5	− 1.9
1020	6408	188	200	−12	191.1	191.7	− 0.6
1084	6812	197	206	− 9	197.6	198.3	− 0.7
1157	7270	205	211	− 6	203.1	204.5	1.4
1250	7854	214.5	220	− 5.5	210.6	212.0	1.4
1846	11600	254	256	− 2	261.3	263.0	1.7

For the bipolar "watch-case," at 20° C, and with 0.3 volts applied,

$$R = 81.4 + 0.0214\,\omega - 0.505 \times 10^{-6}\omega^2. \qquad \text{ohms.} \quad (2)$$

In these equations, 71 and 81.4 are the respective resistances of the two instruments to steady currents; the other constants of each

equation were determined by using two of the observed points on each of the resistance-frequency curves.

Another more interesting fact, obtainable from the experimental curves, is that the product of the damped resistance by the damped

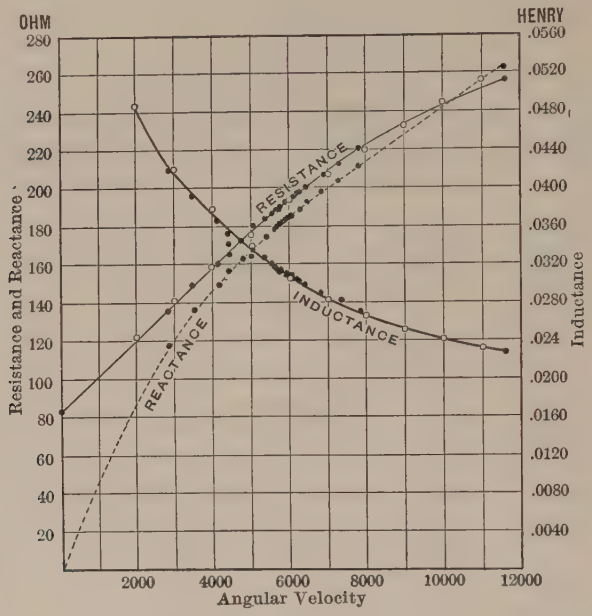

FIGURE 3. Curves of damped resistance, inductance, and reactance *vs.* angular velocity, for watch-case receiver, with 0.3 volt at terminals. Dots, observed; circles calculated.

inductance, for each of the two telephones, is approximately a constant independent of the frequency. That is, for the bipolar "R_b," at 0.3 volt,

$$L = \frac{6.25}{R} \quad \text{henrys} \quad (3)$$

and for the "watch-case" at 0.3 volt

$$L = \frac{5.88}{R} \quad \text{henrys.} \quad (4)$$

The degree of accuracy with which these formulas accord with the observations is shown by the damped resistance and inductance

curves of Figures 2 and 3, where the observed points are indicated by black dots, and the points calculated from the formulas are represented by the circles. The agreement between the calculated points and the curve of observations in the case of the watch-case instrument (Figure 3) is within about 1%. In the case of the Bell instrument "R_b," in

TABLE V.

RESISTANCE AND REACTANCE OF EXPERIMENTAL MONOPOLAR RECEIVER, WITH 0.3 VOLT AT TERMINALS OF RECEIVER.

Frequency.		Resistances.			Reactances.		
n.	$\omega = 2\pi n$.	Free R'.	Damped R.	Motional $R' - R$.	Free X'.	Damped X.	Motional $X' - X$.
993	6240	158	140	18	394	365.3	28.7
1012	6360	321	143	178	354	375.8	− 21.8
1016	6390	266	142	124	427	374.5	52.5
1018	6400	161	142	19	408	378.5	29.5
1020	6410	207	142	65	256	375.8	−119.8
1020	6410	195	143	52	429	378.3	50.7
1023	6428	248	144	104	434	378.2	55.8
1023.6	6436	291	143	148	416	380.6	35.4
1024	6454	211	143	68	432	380.5	51.5
1024	6454	175	143	32	421	382.4	38.6
1024	6435	148	144	4	299	380.0	− 81
1024.2	6440	303	143	160	389	380.0	9.0
1024.8	6444	331	143	188	341	380.4	− 39.4
1025.4	6448	321	143	177	333	380.7	− 47.7
1026	6450	291	143	148	273	380.3	−107.3
1029	6460	238	144	94	257	381.5	−124.5
1032	6480	135	144	− 9	320	380.3	− 60.3
1035	6508	175	144	31	271	383.0	−112
1048	6586	146	144	2	307	387.7	− 80.7
1051	6603	134	144	− 10	340	389.5	− 49.5
1054	6624	140	145	− 5	321	388.7	− 67.7

order to have sufficient range of frequency, the writers had to use some of the earliest observations, taken before they had learned the precautions required for accurate results. But in this case also, the values calculated by the formulas (1) and (3) agree closely with the curves that best represent the observed points except in regions where the latter are uncertain.

As a further illustration of the approximate constancy $R \times L$ taken with the telephone damped, reference is made to Table VII, which contains this product at different frequencies for receiver R_b with 0.42

volt at its terminals. At this voltage, the product for this telephone averages 6.21, and within the range of frequencies between 428 and

TABLE VI.

RESISTANCE AND REACTANCE OF EXPERIMENTAL BIPOLAR RECEIVER PROVIDED WITH EXPLORING COILS, WITH 1 VOLT AT TERMINALS.

Frequency.		Resistance, Ohms.			Reactance, Ohms.		
n. Cycles per Second.	ω. Radians per Second.	Free R'.	Damped R.	Motional $R' - R$.	Free X'.	Damped X.	Motional $X' - X$.
1007	6370	39.4	38.3	1.1	153.7	151.8	1.9
1020	6410	42.7	38.6	4.1	156.1	152.9	3.2
1020	6410	41.2	39.2	2.0	155.1	152.5	2.6
1023	6430	44.0	38.7	5.3	156.2	153.0	3.2
1026.5	6450	50.0	38.8	11.2	149.7	153.6	−3.9
1027	6450	42.0	39.0	3.0	156.5	153.6	2.9
1027	6450	48.6	38.8	9.8	153.6	153.9	−0.3
1027	6452	49.0	38.8	10.2	149.7	153.6	−3.9
1027.5	6455	49.0	38.8	10.2	148.0	153.9	−5.9
1028	6458	47.0	39.0	8.0	147.2	153.7	−6.5
1030	6470	43.0	39.0	4.0	157.4	154.1	3.3
1030	6470	48.2	38.8	9.4	148.8	154.0	−5.2
1033	6492	47.2	38.9	8.3	147.4	154.6	−7.2
1033	6492	46.0	39.0	7.0	156.5	154.5	2.0
1033	6492	50.2	38.9	11.3	154.6	154.3	0.3
1036	6510	44.8	39.0	5.8	158.2	154.9	3.3
1036	6510	46.0	39.0	7.0	148.6	155.2	−6.6
1037	6520	46.0	39.0	7.0	150.0	155.3	−5.3
1038	6525	44.0	39.0	5.0	148.4	155.6	−7.2
1039	6530	50.0	39.0	11.0	151.7	154.6	−3.9
1039	6530	44.0	39.0	5.0	149.1	156.0	−6.9
1039.5	6533	43.0	39.0	4.0	148.4	155.6	−7.2
1041	6540	42.0	39.0	3.0	148.5	155.7	−7.2
1042	6546	48.0	39.0	9.0	149.8	155.7	−5.9
1042	6546	40.2	39.1	1.1	149.3	155.9	−6.6
1043	6560	41.0	39.0	2.0	150.0	156.6	−6.6
1045	6570	40.0	39.0	1.0	150.5	156.8	−6.3
1047	6580	39.0	39.0	0.0	150.7	156.7	−6.0
1051	6600	39.9	39.3	0.6	151.3	157.2	−5.9
1051	6604	38.9	39.3	− 0.4	152.5	156.8	−4.3
1054	6624	39.0	39.3	− 0.3	153.0	158.0	−5.0
1059	6660	38.8	39.3	− 0.5	155.2	158.5	−3.3
1064	6686	38.8	39.6	− 0.8	155.2	159.2	−4.0
1084	6812	39.0	39.6	− 0.6	159.0	161.7	−2.7

890 cycles per second, the product does not depart from the average by more than 2%. There is no march of the product within this range.

When, however, the computation is extended to a single observation at 2464 cycles per second, a departure of 5% is obtained.

A third interesting fact shown by the experimental tables is that the damped reactance is approximately equal to the damped resistance for the telephone "R_b" over a wide range of frequency. This may be seen, for this telephone, at 0.3 volt, by a reference to Figure 2 and by a comparison of the observed reactance values, marked by *crosses*, with the observed points on the resistance curve marked by black *dots*. The damped reactances and damped resistances are seen to be nearly the same throughout the range of frequencies between 451 cycles per second ($\omega = 2834$) and 1250 cycles per second ($\omega = 7850$). Within this range the damped resistance and the damped reactance both nearly double and yet remain within a few percent of equality with each other. For the telephone R_b at 0.42 volts, the same approximate equality holds within the range of frequencies between 428 and 2464 cycles per second, as may be seen by a reference to the fourth and seventh columns of Table III. It is to be noted, however, that this same equality cannot persist at low frequencies, for the damped reactance at zero cycles is zero, while the resistance of this instrument at zero cycles is 71 ohms. As a corollary, it may be observed that within the range of equality of damped resistance and damped reactance, the damped angle of lag of current behind impressed e. m. f. is 45°, and the damped impedance is $\sqrt{2}R$. With the other instruments tested, the equivalence of damped reactance and damped resistance was not obtained; but, as may be seen by reference to Figure 3, the curves of damped reactance and damped resistance for the watch-case instrument run nearly parallel and within 10 ohms of each other, for a considerable range of frequencies.

It would be interesting to discuss the relations expressed in equations (1), (2), (3), and (4). Since, however, at this time the primary purpose of the writers is to present an account of the effects of the motion of the diaphragm in modifying the resistance and reactance of the telephone receivers, a further discussion of the relations (1) to (4) will be deferred.

The Effects of Motion of the Diaphragm on the Resistance and Reactance of the Receivers.— As stated in the introduction, the motion of the diaphragm of a telephone receiver has a marked effect on its resistance and reactance. This effect is best shown by subtracting the damped resistance from the free resistance, and the damped reactance from the free reactance and plotting the differences, called respectively *motional resistance* and *motional reactance*, against

the frequency in radians per second (angular velocity). This is done in Figures 4, 5, and 6. Taking Figure 4 plotted from Table IV obtained with the watch-case receiver, as typical, it will be seen that the Figure contains curves of motional resistance, motional reactance, motional power, and phase angle of motional impedance, marked respectively *Resistance*, *Reactance*, *Power* and *Phase*. These quantities are all plotted against angular velocity. The black dots are observed points, and the circles are computed values, or derived values. Beginning with the resistance curve, and remembering that this curve represents the excess of free resistance over damped resistance, that is to say, the effect of the motion, it will be seen that, starting at a value slightly below zero at 2834 radians per second, the increment of resistance due to motion (motional resistance) increases up to 23 ohms at angular velocity 5674, then descends rapidly to minus 25 ohms at angular velocity 5938 and then increases again toward zero. The motion of the diaphragm markedly increases the resistance at certain frequencies and markedly decreases it at other frequencies. The formulas for computing the motional resistance values are given under heading V below.

Next, let us examine the motional reactance curve. The effect of the motion of the diaphragm is chiefly to decrease the reactance so that the free reactance is less than the damped reactance, giving usually a negative motional reactance, amounting to — 44.7 ohms at angular velocity 5800. The motional reactance is not always negative but shows small positive values in the neighborhood of angular velocities 4500 and 7000.

The resemblance of the motional resistance curves and the motional reactance curve of Figures 4, 5, and 6 to the curves of optical index of refraction and optical absorption plotted against frequency, in the neighboring of an absorption band, will at once strike the attention of the reader familiar with theoretical optics. A difference, however, exists on account of the hysteretic behavior of the iron in the telephone theory, as will be pointed out in the treatment under heading V below.

Effect of Motion of Diaphragm on Draft of Power.— Attention is next directed to the curve marked *Power* in Figure 4. This curve shows the excess of power sent into the telephone when freely vibrating over the power sent into it under the same impressed e. m. f. when damped. The excess of power (i. e. *motional power*) is plotted in microwatts against angular velocity of impressed e. m. f., and is seen to be different for different angular velocities corresponding to different frequencies. The maximum of motional power is in the neighborhood

of angular velocity 5820 radians per second, and this is the period of the diaphragm, as is shown later by other methods of analyzing the data. The impressed e. m. f. in this experiment was maintained throughout at 0.3 effective volt.

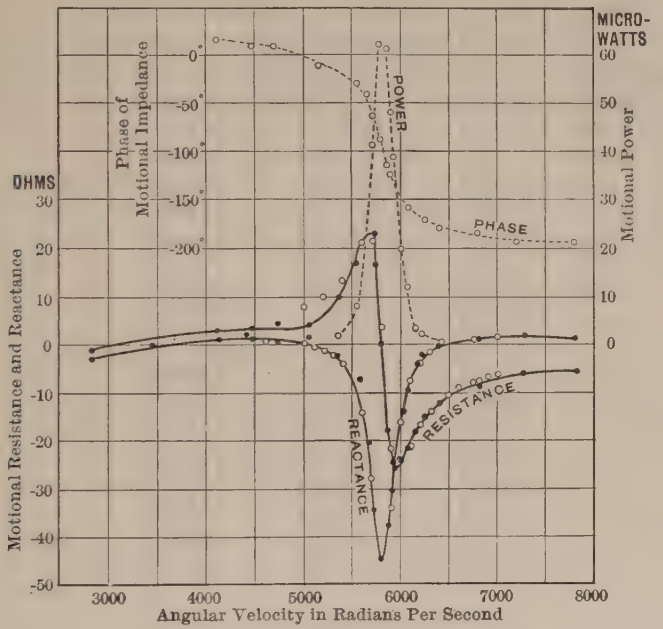

FIGURE 4. Curves of motional resistance, reactance, power, and phase, plotted against angular velocity, for watch-case receiver at 0.3 volt. Dots, observed; circles calculated.

The method of obtaining the motional power curve was as follows: Table III contains measurements of resistance and reactance of this receiver at different frequencies both while free and while damped. The square root of the sum of the squares of resistance and reactance gives directly the impedance. Dividing the impedance into the e. m. f. gives the effective current. The square of the free effective current multiplied by the free resistance gives the free power. Likewise, the square of the damped current multiplied by the damped resistance gives the damped power. The free power minus the damped power gives the *motional power*. These are tabulated for two receivers, for three series of measurements, in Tables VIII, IX and X.

It is not necessarily true that all of the motional power goes into energy of motion. The term means merely the excess of input when

TABLE VII.

SHOWING PRODUCT OF R AND L FOR BIPOLAR RECEIVER R_b WITH 0.42 VOLT AT TERMINALS.

Frequency Cycles per Second. *n.*	Damped Resistance *R.* Ohms.	Damped Inductance *L.* Henry.	*RL.*	Departure. Per cent.
766	174	.0357	6.21	.0
778	175	.0354	6.20	.1
792	176	.0356	6.26	.8
805	177	.0351	6.22	.1
822	181	.0347	6.28	1.0
836	181	.0342	6.19	.3
853	183	.0342	6.26	.8
870	185	.0337	6.24	.5
890	186	.0335	6.23	.2
754	175	.0362	6.33	2.0
744	171.5	.0364	6.24	.5
733	170	.0369	6.26	.8
722	172	.0372	6.20	.1
710	167.5	.0373	6.25	.7
704	168	.0376	6.31	1.6
548	145.7	.0419	6.11	1.6
428	128.5	.0463	6.20	.1
2464	306.5	.0192	5.90	5.0
	Average		6.21	

sounding over input when damped. As a matter of fact, the motional power is negative at some frequencies, as is shown in some of the curves

(e. g. Figures 5 and 6). Always, however, at consonance of the impressed e. m. f. with the period of the diaphragm, the motional power

TABLE VIII.

VALUES OF POWER. BELL BIPOLAR R_b AT 0.3 VOLT.

Frequency.		Power in Microwatts.		
n, Cycles per Second.	ω, Radians per Second.	Free.	Damped.	Motional.
440	2760	325.1	308.7	16.4
512	3220	301.4	303	− 1.6
600	3770	290.5	297.0	− 6.5
670	4210	274.2	283.2	− 9.0
704	4420	270.0	275.0	− 5.0
720	4520	272.7	271.8	.9
744	4660	282.0	266.2	15.8
754	4730	288.8	265.2	23.6
770	4830	304.5	261.0	43.5
778	4880	373.9	262.4	111.5
780	4900	356.9	266.2	90.7
790	4960	438.5	259.2	179.3
792	4970	436.0	259.8	176.2
792	4970	433.0	270.0	163.0
792	4970	423.3	259.2	164.1
793	4975	438.0	260.2	177.8
794	4980	428.0	259.0	169.0
804	5050	364.3	259.2	105.1
808	5080	422.2	257.3	164.9
822	5160	310.4	256.7	53.7
824	5180	371.5	254.0	117.5
824	5180	365.9	250.0	115.9
826	5190	352.0	253.0	99.0
826	5190	376.5	253.0	123.5
832	5220	309.0	260.0	49.0
840	5280	276.7	253.8	22.9
868	5450	269.2	230.6	38.6
890	5590	257.1	241.9	15.2
892	5600	257.1	244.2	12.9
912	5730	244.3	233.3	11.0
940	5900	244.2	239.6	5.6
1000	6283	222.2	220.1	2.1
1060	6650	215.1	213.0	2.1
1152	7250	192.0	190.5	1.5
1248	7850	195.7	197.5	− 1.8
1648	10350	177.4	187.3	− 9.9
2468	15500	153.3	152.1	1.2

has a large positive value, which is no doubt correlative with the large amount of sound produced under this condition. With the receiver

giving the curves of Figure 4 (the bipolar watch-case — cf. Table X) the motional power at resonance is 62 microwatts, which is 20% of the total free input (309 microwatts) and 25% of the total input at the same voltage with the diaphragm damped (247 microwatts). In the case of the bipolar Bell receiver R_b at 0.3 volt (see Figure 5 and

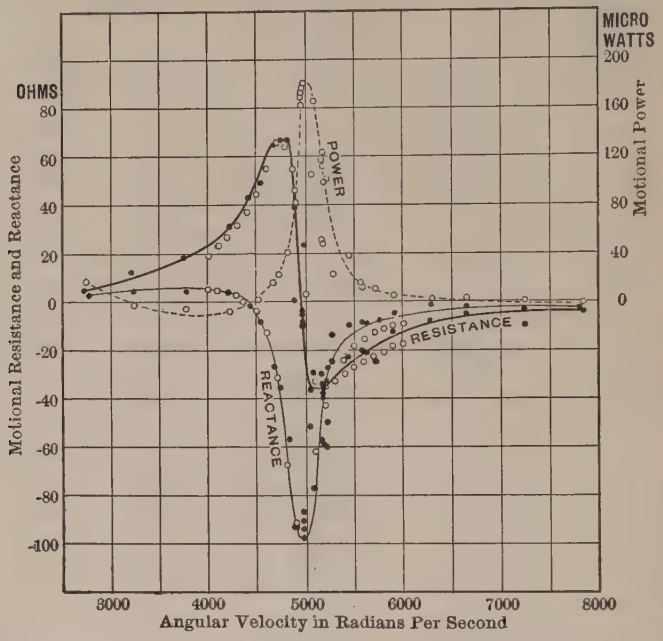

FIGURE 5. Curves of motional resistance, reactance, and power, *vs.* angular velocity, for Bell bipolar, with 0.3 volt. Dots, observed, circles calculated.

Table VIII) the motional power at resonance was 179 microwatts, which is 41% of the free input and 69% of the damped input. At 0.42 volt with receiver R_b (see Figure 6 and Table IX) the motional power was 338 microwatts at resonance, amounting to 40% of the total power input with diaphragm free and to 68% of the power input under the same e. m. f. with the diaphragm damped. That is to say, if one holds his finger on the diaphragm so as to damp it, and measures the power supplied to this receiver at 0.42 volt, the frequency being resonant with the period of the diaphragm, and then takes his finger off, the telephone emits a loud sound and the power input jumps up 68%.

An examination of the curves of Figures 4, 5, and 6 shows how this occurs. The effective resistance of the receiver, with the e. m. f. at resonance, is not very different when it is sounding and when it is damped; that is, the motional resistance is nearly but not quite zero. What causes the large consumption of power at the resonant frequency

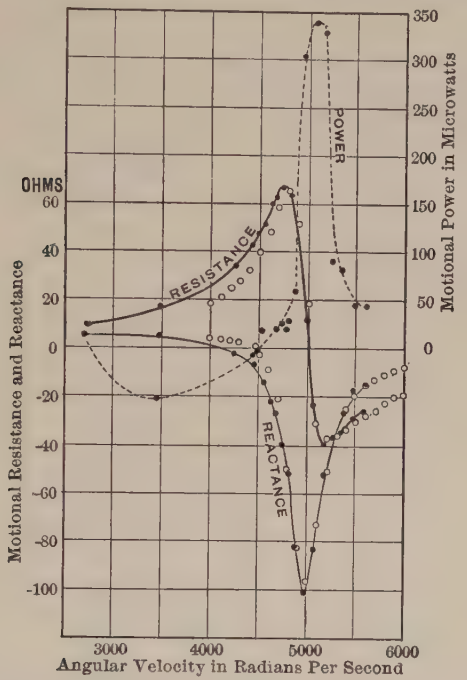

FIGURE 6. Same as Figure 5, but with 0.42 volt at terminals of Bell bipolar. Power points, calculated; other dots, observed; circles, calculated.

is the low value of the effective inductive reactance of the receiver at this frequency and the consequent large draft of current from the source. As we go away from the frequency of e. m. f. resonant with the period of the diaphragm, the motional power consumption may be due either to excess of free resistance over damped resistance or to the excess of free current incidental to a decrease of inductance by the motion.

Effect of Motion on Phase.— The phase angle of the motional impedance for the watch-case receiver is shown in the curve marked

Phase in Figure 4. The angles plotted in this curve were obtained by taking the antitangent of the ratio of motional reactance to motional

TABLE IX.

VALUES OF POWER. BELL BIPOLAR R_b AT 0.42 VOLT.

Frequency.		Power in Microwatts.		
n, Cycles per Second.	ω, Radians per Second.	Free.	Damped.	Motional.
428	2690	677	666	11
548	3446	556	609	− 53
704	4425	520	530	− 10
710	4468	527	528	− 1
722	4540	539	520	19
733	4610	539	518	21
744	4680	546	518	28
754	4740	538	518	20
766	4810	541	512	29
778	4885	570	511	59
792	4976	800	496	304
805	5060	833	495	338
822	5170	825	493	332
836	5253	587	495	92
853	5354	564	481	83
870	5470	524	478	46
890	5595	518	471	47

resistance and plotting the result, which is phase of motional impedance, against angular velocity. The meaning of this phase angle will be made plainer in the discussion of the circular graphs to follow.

Application to Sound Experiments.— It may be noted, in pass-

ing, that the effect of the reaction of the motion of the diaphram in modifying the electrical properties of the telephone receiver is of importance in experiments on sound, where an electrically driven tuning fork or telephone is used as the source of sound, because the power consumed in producing the sound may change with the change of the

TABLE X.

VALUES OF POWER. WATCH-CASE RECEIVER AT 0.3 VOLT.

Frequency.		Power in Microwatts.		
n, Cycles per Second.	Radians per Second.	Free.	Damped.	Motional.
451	2834	396	376	20
550	3456	328	330	− 2
653	4102	302	299	3
702	4410	276	280	− 4
712	4474	284	285	− 1
754	4738	274	274	0
804	5052	264	268	− 4
849.5	5340	258	256	2
884	5554	259	251	8
903	5674	271	250	21
913	5736	290	249	41
923	5800	309	247	62
934	5868	305	244	61
940	5906	291	243	48
945	5938	282	243	39
957	6014	261	241	20
968	6082	252	240	12
980	6158	244	241	3
993	6240	241.5	239	2.5
1020	6408	235	234	1
1084	6812	228	227	1
1157	7270	222	219	3
1250	7854	214	212	2
1846	11600	174	172	2

stationary sound-wave system in the room. In our experiments, the sound emitted from the test telephone was reflected from the various walls of the room and formed a stationary system with nodes and loops at various parts of the room. As an assistant walked about the room while the measurements were being made, it was found that the bridge, previously balanced, was thrown successively in and out of balance as the reflection and absorption of the assistant's clothing

changed the stationary sound system when he walked through the room. Professor Sabine, in some experiments not yet published, had previously noticed the effect of a shift in the stationary wave system in modifying the draft of power by an electrically-driven tuning fork kept vibrating at constant amplitude. In accordance with the present experiments and as Professor Sabine previously suggested in

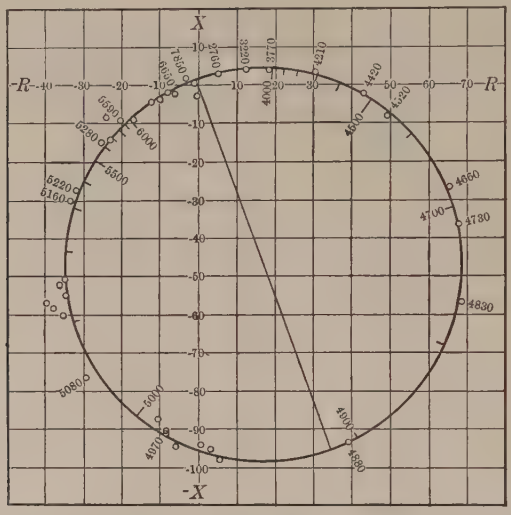

Figure 7. Circular graph for bipolar Bell receiver R_b with 0.3 volt at terminals. Diameter 103 ohms. Depression angle (2β) 70.5°. $\omega_0 = 4885$ radians per sec. $\Delta = 200$. Small circles observed. Internal ring numbers computed.

conversation with one of the writers, the phenomenon is seen to have its explanation in the change of resistance and reactance of the coil of the fork due to the variously affected motion of the fork.

Circular Graphs of Motional Impedance.— A very interesting result is obtained by plotting the motional reactance of a telephone as ordinate against the motional resistance as abscissa. The result is a point on the $R\,X$ plane, and the point is different for different values of the angular velocity used in the measurement. The locus of this point, as the angular velocity is varied, is a circle passing through the origin; that is, through the point of zero motional resistance and zero motional reactance. Stated otherwise, if the motional impedance, $(R' - R) + j(X' - X)$, is plotted vectorially from a point as origin,

the vector for any given frequency is the cord of a circle through the point. As the angular velocity of the impressed e. m. f. increases from zero to infinity, the free end of the vector impedance passes once around the circle. Circular graphs of this character are plotted in Figures 7 to 11 for different instruments or for different values of impressed

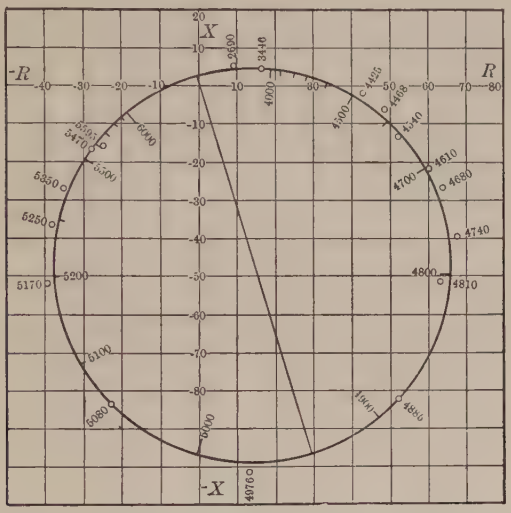

FIGURE 8. Circular graph for bipolar Bell receiver R_b with 0.42 volt at terminals. Diameter 103.5 ohms. Depression angle (2β), 73°; $\omega_0 = 4940$ radians per second; $\Delta = 200$. Small circles observed. Internal ring numbers computed.

e. m. f. These several circular graphs are on different scales, and are summarized to the same scale in Figure 12.

On each of the circular graphs, all of the observed points, for a given receiver with a given impressed e. m. f., are plotted as small circles. The measured angular velocities of the impressed e. m. f. for the observed points are printed at the *outside* of the circular locus. To avoid crowding, not all of the points are designated with angular velocities, and in the selection of the points to bear numerical designation of angular velocity, those points were chosen, for which the measurements were made with especial precaution as to voltage and frequency.

The numbers placed *inside* of each of the circular loci are computed values for the theoretical distribution of angular velocities around

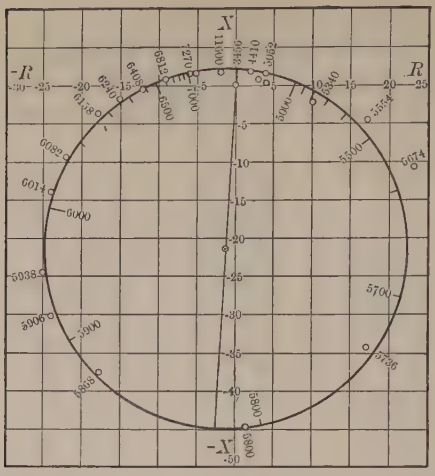

FIGURE 9. Circular graph for watch-case receiver with 0.3 volt at terminals. Diameter 47 ohms. Depression angle (2β) 93°. $\omega_0 = 5820$ radians per second. $\Delta = 150$. Small circles observed. Internal ring numbers computed.

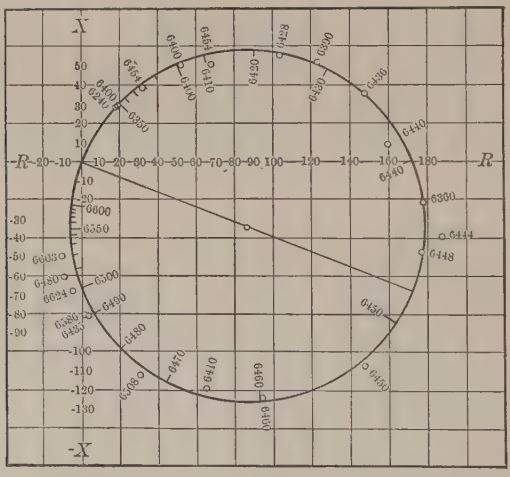

FIGURE 10. Circular graph for experimental monopolar receiver, with 0.3 volt at terminals. Diameter 185.4 ohms. Depression angle (2β) 21.5°. $\omega_0 = 6448$ radians per second. $\Delta = 20$. Small circles observed. Internal ring numbers computed.

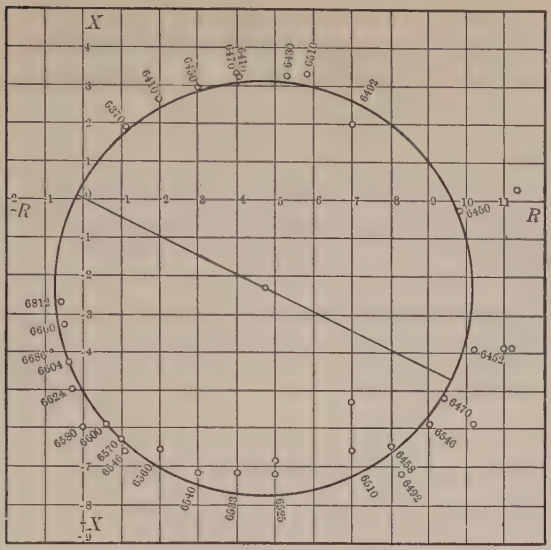

FIGURE 11. Circular graph for experimental bipolar receiver, with one volt at terminals. Diameter 10.9 ohms. Depression angle (2β) 26.5°. $\omega_0 = 6465?$; $\Delta = 20?$.

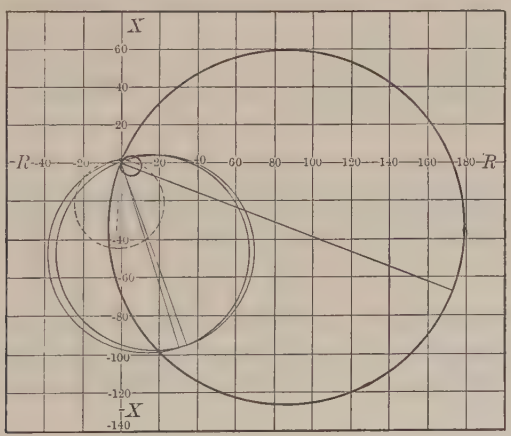

FIGURE 12. Circular graphs collected to one and the same scale. The largest circle and the smallest circle are graphs with experimental receivers. Two light circles near together are graphs with bipolar Bell receiver. Broken circle is graph with watch-case.

the circular graphs. The formulas by which this distribution has been computed are derived under heading V below.

The quantities of theoretical and practical importance in these circular graphs are:

1. The length of diameter of the circular graph for a particular receiver.
2. The dip of the diameter below the axis of resistance.
3. The rate of change of angular velocities around the circle.
4. The angular velocity at the end point of the diameter, remote from the origin, and
5. The impedance at this point.

The significance of these several quantities will appear in connection with the discussion of the theory of the problem, which follows.

V. Theory of the Reactive Effects of Motion of the Diaphragm on the Electrical Constants of the Receiver.

An exact treatment of the electrical properties of a coil containing a magnetic core in proximity to a moving magnetic membrane offers great difficulty. If, however, we confine our attention to terms of the first order, we can obtain a sufficiently close approximation to a solution, to permit an interpretation of the preceding experimental results.

Assumptions Regarding Mechanical Magnitudes.— To this end we shall assume, so far as concerns the fundamental mode of vibration of the diaphragm,

(1) That the elastic restoring force of the diaphragm is all concentrated at the center of the diaphragm, and is proportional to the displacement;

(2) That the motion is opposed by a frictional force proportional to the velocity and also concentrated at the center of the diaphragm; and

(3) That the actual distributed mass of the diaphragm may be replaced by an equivalent mass concentrated at the center of the diaphragm.

Motion of the Center of the Diaphragm under a Pull Maintained Sinusoidal.— As a first step toward the solution, let us assume the diaphragm to be solicited by a force which is maintained sinusoidal; then (*cf.* Figure 13)

$$sx + r\dot{x} + m\ddot{x} = f = Fe^{j\omega t} \qquad {}^{2}\text{dynes} \angle \qquad (5)$$

[2] The sign $\angle$ following the unit indicates that the equation should be interpreted vectorially, or in complex quantities.

in which

x = the displacement of the effective mass of the diaphragm from its position of rest (cm.),

$\dot{x}$ = the displacement velocity (cm/sec),

$\ddot{x}$ = the displacement acceleration (cm/sec^2),

s = the elastic force per unit displacement (dynes/cm),

r = the resisting force per unit velocity (dynes per cm. per sec.),

$f = Fe^{j\omega t}$, the impressed moving force measured in the direction of x toward the poles (dynes),

$\omega = 2\pi n$, the angular velocity of the impressed force (radians per second), and

n = the frequency of the impressed sinusoidal force (cycles per second).

$j = \sqrt{-1}$

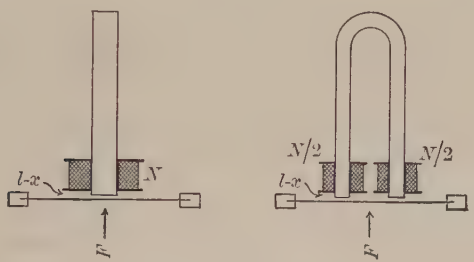

FIGURE 13. Diagram of receivers. N is number of turns. F is force on diaphragm with direction of arrow; l is normal gap length; and x displacement toward poles.

The solution of equation (5) for velocity of displacement, after a steady state has been attained, is well known, and may be written in the form

$$\dot{x} = \frac{f}{r + j\left(m\omega - \frac{s}{\omega}\right)} = \frac{f}{z} = \frac{Fe^{j\omega t}}{z} \quad \text{cm/sec} \angle \quad (6)$$

in which

$$z = r + j\left(m\omega - \frac{s}{\omega}\right) \quad \text{dyne sec/cm} \angle \quad (7)$$

The quantity z may be called "vector mechanical impedance" from its analogy to vector electrical impedance.

We may further write for abbreviation

$$|z| = \sqrt{r^2 + \left(m\omega - \frac{s}{\omega}\right)^2} \quad \text{dyne sec/cm} \quad (8)$$

and

$$\alpha = tan^{-1}\left(\frac{m\omega - \frac{s}{\omega}}{r}\right) \quad \text{radians} \quad (9)$$

The quantities entering in the above equations, and their analogous electrical quantities, are tabulated below.

Mechanical Quantity.		Electrical Quantity.	
Velocity of displacement	$\dot{x}$	i	Current
Mechanical force	f	e	Electromotive force
Resistance (i. e., force of resistance per unit velocity)	r	R	Resistance (i. e., e. m. f. of resistance per unit current)
Effective mass (i. e., force per unit time-rate of change of velocity)	m	L	Self-inductance (i. e., e. m. f. per unit time-rate of change of current)
Elastic force per unit displacement (i. e., per unit time-integral of velocity)	s	$1/C$	Reciprocal of capacity (i. e., e. m. f. per unit time-integral of current)
Vector mechanical impedance	z	Z	Vector electrical impedance
Mechanical Impedance	$\|z\|$	$\smile$	Electrical impedance
Mechanical phase-angle	α	θ	Electrical phase angle
Mechanical inertia reactance	$m\omega$	$L\omega$	Electrical inductive reactance
Mechanical elastic reactance	s/ω	$(1/C\omega)$	Electrical capacity reactance

Circular Graph of Velocity.— By equation (6) $\dot{x}$ is seen to be sinusoidal, with amplitude $\frac{F}{|z|}$ and lagging by an angle α behind the impressed force. A geometrical representation of the amplitude and phase of $\dot{x}$ is given in Figure 14. In the left hand part of the figure Op is a representation of the vector mechanical impedance z. As ω changes from zero to infinity, the point p moves along the straight line Xp from minus infinity to plus infinity, parallel to OY. In the right hand part of the figure, the circle is the vector graph of F/z, which is given in magnitude and direction by OP. This circle is obtained by taking the reciprocal of the straight line locus of the vector

z and multiplying the reciprocal by F, which gives a circle of diameter F/r symmetrically disposed with reference to the axis of reals.

The use of this circle is as follows. For a given value of ω find the angle α by equation (9) and lay off this angle negatively at O; then the length of the chord OP of the circle gives the amplitude $\frac{F}{|z|}$ of x,

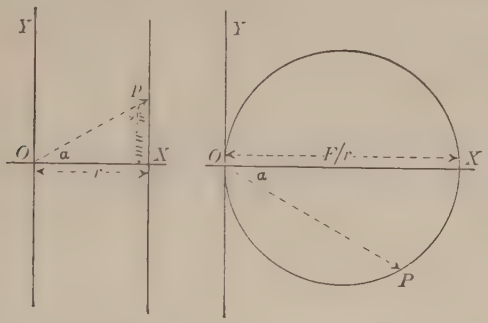

FIGURE 14. Left straight line graph of z. Right, circular graph of F/z.

for the given ω, and the angle is the angle of lag of $\dot{x}$ behind the impressed force. As ω changes from zero to infinity, the point P moves negatively once around the circle from O, through X, back to O.

Magnetic Flux as Dependent on Current and Mechanical Displacement.— In the problem under consideration, the pull f acting on the diaphragm is determined by the magnetic flux through the air gap, or air gaps, of the receiver. If ϕ is the mean flux through the active part of the magnetic circuit, we have, for a bipolar receiver, approximately

$$\phi = \frac{\mathfrak{F}}{\mathfrak{R}} = \frac{\mathfrak{F}_0 + 4\pi Ni}{\mathfrak{R}_0 + \dfrac{2\,(l - x)}{S}} = \mathfrak{B}\,S \qquad \text{maxwells} \quad (10)$$

and for a monopolar receiver, approximately

$$\phi = \frac{\mathfrak{F}}{\mathfrak{R}} = \frac{\mathfrak{F}_0 + 4\pi Ni}{\mathfrak{R}_0 + \dfrac{l - x}{S}} \qquad \text{maxwells} \quad (11)$$

in which

$\mathfrak{F}$ = the total m. m. f. due to the permanent magnet and to the current i in the coils (gilberts),

$\mathfrak{F}_0$ = m. m. f. due to permanent magnet alone (gilberts),

$\mathfrak{R}$ = total reluctance of the magnetic circuit (oersteds),
$\mathfrak{R}_0$ = reluctance of circuit exclusive of that of the gaps (oersteds),
N = total number of turns in the receiver coils,
i = instantaneous current in the coils assumed to vary sinusoidally, or according to the real part of $Ie^{j\omega t}$ (absamperes),
l = normal air-gap between poles and diaphragm (cm.),
$\mathfrak{B}$ = mean flux density in the air gap (gausses), and
S = area of one gap (cm^2).

The Equations of Current and Motion.— We can now express the pull on the diaphragm in terms of the flux. It is a well known fact, which may be derived from energy relations, that the pull on the diaphragm is

$$f = \frac{\phi^2}{4\pi S} \text{ for a bipolar receiver} \qquad \text{dynes} \quad (12)$$

and

$$f = \frac{\phi^2}{8\pi S} \text{ for a monopolar receiver} \qquad \text{dynes} \quad (13)$$

If now f_i is used to denote the part of the pull due to the current i, and if this is small in comparison with the pull due to the permanent magnet, we may write

$$f_i = \frac{df}{di} i \qquad \text{dynes} \angle \quad (14)$$

which by substitution from equations (12) and (10) becomes

$$f_i = \frac{2\phi}{4\pi S} \frac{d\phi}{di} i$$

$$= \frac{2N\phi}{\mathfrak{R}S} i = \frac{2N\mathfrak{B}_0}{\mathfrak{R}} i \text{ for a bipolar} \qquad \text{dynes} \angle \quad (15)$$

and

$$f_i = \frac{N\mathfrak{B}_0}{\mathfrak{R}} i \text{ for a monopolar.} \qquad \text{dynes} \angle \quad (16)$$

In equations (15) and (16) $\mathfrak{B}_0$ has been substituted for $\mathfrak{B}$, since the increment in $\mathfrak{B}_0$ due to i, when multiplied by i, is assumed to be a second order effect.

In order to avoid carrying through separate discussions for the

bipolar and for the monopolar receiver, and in order to simplify the equations, let us write

$$A = \frac{2N\mathfrak{B}_0}{\mathfrak{R}} \text{ for the bipolar receiver, and} \qquad \text{dynes/absampere} \quad (17)$$

$$A = \frac{N\mathfrak{B}_0}{\mathfrak{R}} \text{ for the monopolar receiver;} \qquad \text{dynes/absampere} \quad (18)$$

then, for either instrument,

$$f_i = Ai \qquad \text{dynes} \angle \quad (19).$$

Equations (15), (16) and (19) assume that the pull on the diaphragm due to i is in the phase with i; but with hysteresis and eddy currents present, the electromagnetic force will lag[3] behind the current i by an angle β_1; whence the force on the diaphragm due to the current i becomes, by eq. (19),

$$f_i = A\, i\, \angle\beta_1 \qquad \text{dynes} \angle \quad (20)$$

Consequently, by equation (6),

$$\dot{x} = \frac{A\, i\, \angle\beta_1}{z} \qquad \text{cm/sec} \angle \quad (21)$$

The e. m. f. induced in the coils by the motion of the diaphragm will be, in the absence of hysteresis,

$$e_x = N\frac{d\phi}{dt} = N\frac{\partial\phi}{\partial x}\dot{x} \qquad \text{abvolts,} \angle \quad (22)$$

and by differentiating equation (10) or (11), equation (22) gives to a first approximation

$$e_x = \frac{2N\mathfrak{B}_0\dot{x}}{\mathfrak{R}} = A\dot{x} \qquad \text{abvolts,} \angle \quad (22a)$$

and by substitution from equation (21)

$$e_x = \frac{A^2 i\, \angle\beta_1}{z}. \qquad \text{abvolts} \angle \quad (23)$$

However, it should be noted that there is also a hysteretic lag of flux with change of gap, and this will cause the induced e. m. f. to lag by a certain angle β_2 behind $\dot{x}$, so that equation (23) should be changed to

$$e_x = \frac{A^2 i\, \angle\beta_1 + \beta_2}{z} \qquad \text{abvolts} \angle \quad (24)$$

---

3 On the question of Constancy of β_1 see VI below.

If L and R are the inductance and resistance of the receiver when damped, the impedance of the damped receiver will be

$$Z = R + jL\omega \qquad \text{absohms } \angle \quad (25)$$

and if e is the instantaneous value of the impressed e. m. f. of the type $Ee^{j\omega t}$, we shall have

$$e = iZ \qquad \text{abvolts } \angle \quad (26)$$

But owing to the influence of the e. m. f. of motion, the last equation becomes modified to

$$e - e_x = iZ \qquad \text{abvolts } \angle \quad (27)$$

or

$$e = iZ + e_x \qquad \text{abvolts } \angle \quad (28)$$

That is by equation (24)

$$e = i\left\{ Z + \frac{A^2}{z}\sqrt{\beta_1 + \beta_2} \right\} = iZ' \qquad \text{abvolts } \angle \quad (29)$$

where Z' is the free impedance of the receiver.

This means that the impedance of the receiver has become increased, through the vibration of the diaphragm, by *a motional impedance:*

$$Z' - Z = \frac{A^2}{z}\sqrt{\beta_1 + \beta_2} \qquad \text{absohms } \angle \quad (30)$$

This motional impedance, being the reciprocal of the vector equation of a straight line with ω as variable, is a circle for variable ω, and has a diameter $\frac{A^2}{r}$, depressed below the axis of reals by an angle $\sqrt{\beta_1 + \beta_2}$.

As to the relative values of β_1 and β_2 it seems reasonable that whether the change of flux of a circuit is caused by a small change of current, changing the m. m. f., or by a small change of gap-length, changing the reluctance, the angle of lag of flux behind the cause is the same; that is $\beta_2 = \beta_1 = \beta$ (Say). This is borne out by one of our experiments to be described below (see VI). With this equivalence substituted in equations above, we obtain,

$$Z' - Z = \frac{A^2}{z}\sqrt{2\beta} \qquad \text{absohms } \angle \quad (31)$$

Consequently, if we vary ω from 0 to $+\infty$, keeping the impressed e. m. f. and all other quantities constant, the motional impedance $Z' - Z$ has a circular graph through the origin, with its principal

diameter of length $\frac{A^2}{r}$ depressed 2β below the axis of reals. Equation (31) is the theoretical equation to the circular graphs of Figures 7 to 12.

Replacing the vector z of equation (31) by its absolute value $|z|$ and angle α, we have

$$Z' - Z = \frac{A^2}{|z|} \overline{2\beta + \alpha} \qquad \text{absohms } \angle \quad (32)$$

Equation (32) may be analysed into

$$R' - R = \frac{A^2}{|z|} \cos(2\beta + \alpha) \qquad \text{absohms} \quad (33)$$

$$X' - X = \frac{-A^2}{|z|} \sin(2\beta + \alpha) \qquad \text{absohms} \quad (34)$$

in which

$$|z| = \sqrt{r^2 + \left(m\omega - \frac{s}{\omega}\right)^2}, \qquad \text{absohms} \quad (35)$$

and

$$\alpha = \tan^{-1}\left(\frac{m\omega - \frac{s}{\omega}}{r}\right) \qquad \text{radians} \quad (36)$$

are functions of ω. The quantity A, involving $\mathfrak{B}_0$ and $\mathfrak{R}$, might be expected to vary with variation of ω, but an examination of the experimental results shows that, with the excitations employed, not much error is introduced by considering A and also β independent of ω.

Equations (32), (33), and (34) are in convenient form for computation, and permit an easy determination of some of the important mechanical constants of the diaphragm.

For example, if we let ω_0 be the angular velocity of impressed mechanical force for which the sustained vibration of the diaphragm is in resonance, we see from equation (6) above that

$$\omega_0 = \sqrt{\frac{s}{m}} \qquad \text{radians/sec.} \quad (37)$$

Now, if ω, the angular velocity of the impressed electromotive force in the telephone circuit, is equal to $\omega_0 = \sqrt{\frac{s}{m}}$, it is seen by equation (36)

that a becomes zero; hence the value of ω, which in the experimental circular graphs of Figures 7 to 10 lies at the remote end of the principal diameter is the $\omega = \omega_0$ for which the diaphragm in sustained vibration is resonant. This gives a simple and accurate method of determining ω_0 for a telephone diaphragm.[4]

Again, let Δ be the logarithmic decrement per second of the diaphram, if vibrating under no external force, then by the theory of elasticity,

$$\Delta = \frac{r}{2m}, \qquad \text{numeric/sec.} \quad (38)$$

whence from (36)

$$\omega \tan a = \frac{\omega^2 - \omega_0^2}{2\Delta} \qquad \text{numeric/sec.} \quad (39)$$

Differentiating (39) with respect to a, we obtain

$$\frac{d\omega}{da} \tan a + \omega \sec^2 a = \frac{\omega}{\Delta} \frac{d\omega}{da} \qquad \text{numeric/sec.} \quad (40)$$

and if $a = 0$,

$$\left[\frac{d\omega}{da}\right]_0 = \Delta; \qquad \text{numeric/sec.} \quad (41)$$

That is, in the experimental circular graphs, the rate of change of ω with change of a, at the remote end of the principal diameter, is the logarithmic decrement per second of the diaphragm. This quantity cannot, however, be obtained with the precision with which ω can be obtained.

Another method of obtaining Δ is by taking the values of ω_1 and ω_2 which lie respectively 45° below and 45° above the principle diameter,— these angles being measured at the origin, not at the center. For these points tan a is respectively + 1 and — 1; whence from (39)

$$2\Delta\omega_1 = \omega_1^2 - \omega_0^2$$
$$-2\Delta\omega_2 = \omega_2^2 - \omega_0^2$$

and by subtraction and division by $2(\omega_1 + \omega_2)$,

$$\Delta = \frac{\omega_1 - \omega_2}{2} \qquad \text{numeric/sec.} \quad (42)$$

[4] For another method of finding ω_0 from the humming tone of a telephone receiver, see a paper by A. E. Kennelly and W. L. Upson, Proc. Am. Phil. Soc., 1908, "The Humming Telephone."

Thus we have methods of determining both ω_0 and Δ. The experiments, on the other hand, do not permit a direct determination of the quantities m, r, and s; but it would seem that by adding a known mass, as a small load, to the center of the diaphragm and repeating the series of measurements, these quantities should be capable of determination.

VI. Comparison of Experimental Results with Theory.

An examination of the experimental results with the aid of the theory above developed gives the following results, which may be called the characteristics of the several receivers (Table XI):

TABLE XI.

Summary of Characteristics of Receivers.

	Bipolar Bell R_b at 0.3 Volt.	Bipolar Bell R_b at 0.42 Volt.	Watch-case at 0.3 Volt.	Experimental Monopolar at 0.3 Volt.	Experimental Bipolar at 1 Volt.
Diameter of motional impedance circle in ohms.	103	103.5	47	185.4	10.9
Depression angle (2β) in degrees	70.5	73	93	21.5	26.5
ω_0 in radians per second	4885	4940	5220	6448	6465 ?
Log. dec. per second. (Δ)	200	200	150	20.	20 ?

The method of obtaining these characteristics was as follows: The circular graphs of Figures 7 to 11 were plotted. The diameter of the motional impedance circle and the angle of depression of this diameter below the axis of $R'-R$ could be measured off at once on the diagram. The value of ω at the free end point of the diameter could also be read or obtained by interpolation; this ω is the ω_0 of the diaphragm. The logarithmic decrement per second Δ could have been obtained by either of the two methods derived in the discussion of the theory, equations (41) or (42); but a third method was employed; namely, by the use of the more general equation (39), in which several values of a and the corresponding values of ω from the circular graphs were substituted, and the values of Δ so obtained were averaged.

Having now obtained the constants of Table XI, the theoretical distribution of angular velocities around each of the circular graphs of Figures 7 to 11 were calculated by equation (39), and these theoretical values are designated by numerals on the inside of the circular graphs.

The values of $R'-R$ and of $X'-X$ corresponding to these theoretical values of ω were then plotted as the circles on the rectangular graphs of motional resistance and motional reactance in Figures 4, 5, and 6. It is seen that the agreement of the computed and observed points in these Figures 4 to 6, while not exact throughout the entire range, is yet sufficiently good to show that the theory is essentially correct.

Another significant point in the theory is the interpretation we have given to the depression angle 2β of the circular graphs. We interpreted β to be the angle by which the magnetic flux lags behind the magnetizing current in the telephone receivers. To test this point, this angle of lag of magnetic flux behind magnetizing current was independently measured with the experimental bipolar receiver. This receiver had a separate secondary, or exploring, coil wound around the ends of its poles, near the diaphragm. The e. m. f. generated in this exploring coil is in phase with the time rate of change of flux; and the phase of this e. m. f. was compared with the phase of the alternating current in the exciting coils in two ways (1) by a three-voltmeter method and (2) by an alternating current potentiometer.

In the three-voltmeter method, a known resistance was put in series with the exciting coils, and one end of the exploring coil was connected to the point between the exciting coil and the known resistance. With the frequency and the e. m. f. about the telephone kept the same as that used in the bridge measurements (i. e., the e. m. f. of 1 volt, and the frequency near the resonant frequency of the diaphram) voltages were measured about the known resistance (20 ohms), about the exploring secondary, and about the two in series. These voltages, being small, were measured by a crystal rectifier in series with a galvanometer,[5] — the galvanometer and rectifier having been calibrated immediately before and after the experiment by an a. c. potentiometer operating at the frequency employed.

The readings of voltage were very consistent, and were as follows in a typical case:

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[5] G. W. Pierce: Phys. Review, **25**, p. 31, 1907; ibid., **28**, p. 153, 1909.

Voltage about 20 ohms	= 0.129 volt
" about secondary	= 0.125 "
" about both	= 0.196 "
" about both with secondary reversed	= 0.161 "

Substitution of the first three of these values in the formula for an obtuse-angle oblique triangle gives 79°, as the angle by which the secondary voltage leads the primary current. This is the angle by which the time derivative of the magnetic flux leads the primary current. The flux itself lags its time derivative by 90°, and therefore lags the primary current by 90°—79° = 11°.

Again, a substitution of the first, second, and fourth value of above table in the formula for an acute-angle oblique triangle gives for the flux lag angle the value 11.5°.

This angle of lag of flux behind the magnetizing current was found to be nearly independent of the frequency. To illustrate this, and as a further confirmation of the result obtained by the three-voltmeter method with the crystal rectifier and galvanometer as voltmeter, a second measurement was made by an entirely different method; namely, by the use of a Drysdale alternating-current potentiometer, with a 60-cycle current, and with a vibration galvanometer as indicating instrument. The method employed in this experiment consisted in first measuring the magnitude and phase of the primary current, and then the magnitude and phase of the voltage in the secondary winding. The difference between these two phases, subtracted from 90°, gives the required angle of magnetic flux lag. Balance was in each case indicated by getting a zero deflection of the vibration galvanometer. This method gave 12.5° as the angle by which the flux in the telephone lags behind the magnetising current.

The three values obtained by direct measurement for the flux lag, which should be the angle β according to the theory above proposed, are 11°, 11.5°, and 12.5°; whereas half the depression angle, for this telephone, which, according to the theory, should also be the angle β, is 13.2°. The agreement is not as good as might be desired for a perfect confirmation of the proposed theory; but in view of the difficulty of measuring small angles of lag in circuits containing voltages of the order of 0.1 volt, and in view of the fact that the experimental telephone receiver constructed for this purpose had to be complicated by auxiliary secondary windings and also unfortunately had a diaphragm mounted in such a way as to have a very large temperature coefficient of vibration period, which rendered difficult an accurate

determination of the points of the circular graph, the writers believe that the departure of a degree or two in the value of β, as obtained by direct measurement from its value as obtained by the circular graphs, is not unsatisfactory.

VII. Summary of Results.

1. The resistance and inductance of several telephone receivers were measured over a wide range of frequencies with their diaphragms both free and damped.

2. The damped resistance is approximately a quadratic function of the angular velocity of impressed e. m. f. (see equations (1) and (2)).

3. Although the damped resistance and the damped inductance both change with the frequency of e. m. f., their product is approximately constant, independent of the frequency, over a considerable portion of the range of audible frequencies (see eq. (3) and (4) and Table VII).

4. The damped reactance of one form of standard bipolar Bell receiver is approximately equal to its damped resistance, over a considerable range of frequency; so that the current lags the e. m. f. by 45° (see Figure 2).

5. The free resistance and reactance of telephone receivers go through marked changes with changes in frequency of constant e. m. f. in the neighborhood of the natural frequency of their diaphragms (*cf.* Figures 4–6).

6. The motional resistance and motional reactance (by which is meant excess of free resistance of reactance over damped resistance or reactance) conform accurately to certain simple laws as follow:

I. The motional reactance plotted as ordinates against the motional resistance as abscissas, as the frequency of constant impressed e. m. f. is changed from zero to infinity, gives a circular locus, with various interesting characteristics (*cf.* Figures 7–12).

II. The rectangular plots of motional reactance and motional resistance against angular velocity of constant impressed e. m. f. give curves somewhat analogous to the curves of index of refraction and absorption of light in an optical medium in the neighborhood of an absorption band (*cf.* Figures 4–6).

7. The power taken by a telephone receiver when sounding at 0.3 volt applied voltage may exceed by 68% the power taken from the

same e. m. f. when the diaphragm is damped (Figures 4–7 and Tables VIII–X).

8. A theoretical explanation of the phenomena is given, and computations are submitted in comparison of experiment and theory (Headings V and VI).

9. The vibration constants of the diaphragms of the several receivers are deduced and collected (Table XI).

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CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY.

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Introduction.

This paper is in the nature of a supplement to a former paper on the properties of water in the liquid and the solid forms.[1] The solid forms were studied over a range of 20,000 kgm./cm.^{2}, and from $-80°$ to $+76°$, but the study of the liquid reached only from the lowest temperature of its existence to about $+20°$. Above $0°$, measurements were made on the liquid at only $20°$. The two measurements, at $0°$ and $20°$ were sufficient to give the mean dilatation between $0°$ and $20°$, but not the variation of dilatation with temperature. It was assumed in the earlier paper that the variation of dilatation with temperature became negligible at high pressures, since this seemed to be the most plausible assumption in view of all the data then available.

In this present paper the study of the liquid has been continued from $20°$ to $80°$, and to 12000 kgm. The pressure range is greater than that of the preceding paper by about 2,500 kgm. The range is not great enough to entirely cover the region of stability of the liquid, but it is as great as it was convenient to cover with the method used here, which is different from that of the former work. It has the advantage of very much greater rapidity of operation, but since it depends on the complete elastic integrity of the steel pressure cylinders it is not possible to reach so high pressures with it as with the former method. [The former limit of 9500 kgm. was set by the freezing of the liquid and was not due to any limitation of the method.] Nevertheless, it may be hoped that the present temperature and pressure ranges are both wide enough to give a fairly complete idea of the nature of the effects to be expected at high pressures with varying temperature.

Measurements of the dilatation have been made at four temperatures, so that it has been possible to find the variation of dilatation with temperature at any pressure. Perhaps the most unlooked for feature disclosed by the measurements is the fact, contrary to the assumption of the first paper, that the variation of dilatation with temperature does not become vanishingly small at high pressures, but reverses in sign. This means that while at low pressures the volume increases more and more rapidly with rising temperature, at high pressures the expansion becomes more slow at high temperatures.

The data of this paper are sufficient to completely map out the p-v-t surface over the domain in question: Both the first and second

1 Bridgman, These Proceedings, **47**, 439–558 (1912).

derivatives are therefore completely determined, so that we now have all the data at hand for the determination of any one of the thermodynamic properties of the liquid. This means that we are in a position to find such quantities as the specific heats, change of internal energy, adiabatic temperature rise etc., as well as the more easily determined compressibility and thermal dilatation. The latter part of the paper, after the discussion of the method and the presentation of the data in the first part, is occupied with the computation of these various thermodynamic quantities. The accuracy of some of these is probably not very great, because the error in the second derivative of an experimental quantity may be considerable. It has, therefore, seemed best to give the general view of the nature of the quantities which is offered by a graphical representation, rather than to give tables, with the tacit assumption of greater accuracy which usually goes with a set of tables. In spite of the lower order of accuracy of some of these thermodynamic quantities, it has still seemed well worth while to give them, since even the general trend of some of the quantities, such as the specific heats, has not been hitherto known with relation to pressure.

The data presented here are only the beginning of a projected study of the characteristic surface under high pressures for a number of liquids. The measurements have already been carried through for twelve other liquids beside water. The purpose of this study is ultimately the development of a theory of liquids, since it would seem that a much more intimate grasp of the nature of the forces at work in a liquid would be afforded by a study over a wide pressure range, than over the comparatively low pressures hitherto used. It must be admitted, however, that this broader purpose is not particularly furthered by this work on water, because of the well known abnormalities of this substance. In the previous paper several abnormalities had been shown to exist at low pressures. In this paper, new abnormalities are found at higher pressures. Water gives the appearance of becoming completely normal only at the higher temperatures and pressures of the range used here, but of course whether this is really normal or not cannot be told until the behavior of normal liquids has been discovered. The full significance of the present data, in their bearing on such questions as the polymerization of the liquid, for example, cannot appear until after the discovery of the laws for entirely normal liquids. The investigation of water before that of normal liquids was undertaken for two reasons; firstly because of the desire to complete the work for water already begun, and

secondly because in this and the following investigation a new method for determining the compressibility was to be used, which had not yet been proved to be reliable, but which could be tested by a comparison of the results obtained by this method with those already obtained by another method at lower temperatures for water.

In addition to the data for liquid water, two other quantities were determined incidentally in the course of the work, and are given at the end of the paper. One of these is the experimental measurement of the compressibility and thermal dilatation of ice VI between 0° and 20° and 6360 and 10,000 kgm. The other is the measurement of the volume of kerosene up to 12,000 kgm. and between 20° and 80°.

The Method.

The method in its fundamental idea is as simple as it would well be possible to devise. The substance, whose compressibility or thermal dilatation is to be measured, is placed in a heavy steel cylinder in which pressure is produced by the advance of a piston of known cross section. The change of volume, given by the distance of advance of the piston, is measured as a function of the pressure. The method is simple, rapid, and above all, applicable to the highest pressures. But there are a number of corrections which must be made, often difficult to determine, which doubtless account for the slight use which has been made hitherto of the method. Apparently, with the exception of the present work, it has been used recently only by Tammann,[2] and by Parsons and Cook.[3] Tammann and Parsons and Cook applied it only to the measurement of compressibility, reaching pressures of about 4000 kgm. The author has previously applied it to the measurement of the thermal dilatation of water at temperatures below 0° C. over a pressure range of about 6500 kgm.

The most serious of the errors which readily occur to one is that of leak. It is almost essential to the success of the method to secure a piston absolutely free from leak, and this has hitherto been a matter of some difficulty at high pressures. Tammann did not entirely secure this freedom from leak, but avoided it in large measure by the use of a very heavy oil, such as castor oil, and still further lessened the error by correcting for the slight amount of leak by measuring the amount of liquid which escaped past the piston in a given time. This method would not be applicable to the highest pressures, however, because

[2] A. D. Cowper and G. Tammann, ZS. Phys. Chem., **68**, 281–288 (1909).
[3] Parsons and Cook, Proc. Roy. Soc. A, **85**, 332–349 (1911).

of the freezing of the oil. Parsons and Cook were able to secure entire freedom from leak up to 4000 kgm. by the employment of a cupped leather washer combined with a brass disc of special design. It has been the experience of all those who have worked with high pressures, however, that no leather washer is capable of standing pressures very much in excess of the limit of 4500 kgm., since the leather rapidly disintegrates under the pressure. In the present work the same form of packing was used which was used in the previous work on the freezing of water and mercury under pressure. This has been proved in the previous paper to be absolutely free from leak up to the highest pressures which can be sustained by the steel containing vessels. In the present work this same packing has proved itself to be reliable for the purposes of this method.

The question of the method of measuring pressure is also of considerable importance in using this method, since the usual measuring devices, such as a Bourdon gauge, cannot be applied, for reasons to be discussed later, and attempts to calculate the pressure directly from the force required to produce motion of the piston are likely to be in error because of the friction of the packing. Parsons and Cook did, however, adopt this latter method, and computed the pressure from the known force required to move the piston. The effect of the friction of the packings was allowed for in as large a degree as possible by taking the mean of the readings during increasing and decreasing pressure, assuming that the friction remained constant. The results obtained by Parsons and Cook in this way were surprisingly good. That the friction did remain fairly constant was indicated by the constancy of the results and the fact that the curve nearly always returned to the starting point; but it is doubtful if the method would work at very much higher pressures because of the increase of friction due to the flow of the softer parts of the piston. The brass washers used by Parsons and Cook would almost certainly have upset under two or three thousand more kgm., and it is the experience of the author that it is difficult to obtain even steel washers which will stand much more than 8000 kgm. without taking some set. In fact, at high pressure there must necessarily be some plastic yield, in order to follow the expansion of the cylinder. The result of this set in the washers is that the friction becomes very irregular, and cannot be assumed to be the same during increasing and decreasing pressure. Variations in the amount of friction due to this cause of as much as 200 or 300% have been found at the higher pressures of this work.

The only escape from the difficulty seems to be to measure the

pressure directly inside the cylinder. This was done by Tammann by connecting a Bourdon gauge directly to the cylinder. But it is known that the errors of the Bourdon gauge become rapidly more serious at higher pressures,[4] due to the increase of hysteresis, so that this gauge could not be used for the pressures of this experiment. Furthermore, no Bourdon gauge has up to the present been made of sufficient sensitiveness which is capable of standing more than 6500 kgm. In the present work the pressure was measured inside the cylinder by inserting directly into it a coil of manganin wire, which had been already calibrated against an absolute gauge. This method of measuring pressure has been fully described in a previous paper.[5] It was necessary for the purposes of the present work, however, to make a somewhat more careful determination of the temperature coefficient than was done formerly, and this determination will be described in detail later. The method has shown itself perfectly satisfactory and reliable in every respect. One coil of wire has been used almost continuously for over six months, and occasional calibrations have shown no change. These calibrations were made by measuring with the coil certain fixed temperature-pressure points, such as the freezing pressure of mercury or of ice VI, at some fixed temperature.

The apparatus used in the present work is the same in most features as that used in the former work, a detailed account of which has already been given in the papers mentioned. Only the points in which this has been changed will be mentioned here. It was a disadvantage of the former method that the apparatus consisted of two parts; the lower part, a cylinder containing the liquid to be measured, was placed in a thermostat, and the upper part, a cylinder in which pressure was produced, was exposed to the temperature of the room. When temperature was changed in the thermostat below or pressure was changed in the cylinder above, liquid passed from the one cylinder to the other, experiencing in the transition a change of temperature, and so a change of volume also. This change of volume accompanying a known change of temperature varies in an unknown way with the pressure, and to apply the correction it was necessary to make an independent set of experiments. In the present form of apparatus the difficulty was avoided by including everything in one cylinder. This cylinder contained the liquid under investigation, the pressure measuring coil, and the piston by which pressure was produced. It

4 Bridgman, These Proceedings, **44**, 201–217 (1909).
5 Bridgman, These Proceedings, **47**, 319–343 (1911).

was placed in the lower part of the hydraulic press and, together with the lower part of the press, was placed in the thermostat. The dimensions were so small that this could be done without increasing to an unwieldly bulk the size of the apparatus, the four tie rods of the press being 1 1/8″ in diameter and their centers 6″ apart. It is the same form of apparatus which was used for the measurements on ice VI up to 20,500 kgm. The present experiments run to only 12,000 kgm., however, since it is evidently an absolute essential to the success of the method that there should be no permanent distortion of the cylinder. It would be easily possible to reach pressures much higher than those reached in this experiment, but it was felt that the risk and the extra time involved in the probable construction of new apparatus was not justified at present, when it seemed that the most important work was to map out the field, obtain data for as many liquids as possible, and determine the general nature of the significant problems. Later, if there are crucial points which need the use of much higher pressures, it will be a comparatively easy matter to obtain them.

The cylinder used in this experiment was not the same as that used in the previous work on water. This new cylinder is from a piece of chrome-vanadium steel made in the electric furnace by the Halcomb Steel Co., of Syracuse, N. Y. The steel itself is a wonderful product, and without it the present investigation would not have been so easily possible. It shows a tensile strength of 300,000 lbs. per sq. in. when hardened in oil, and an elastic limit of about 250,000 lbs. These figures are considerably in excess of those for the steel used in the previous investigation. The steel furthermore is remarkably homogeneous, because of its production in the electrical furnace. One of these pieces was pierced with a hole 1/8″ diameter and 13″ long, and the drill came through concentrically without any variation from the straight line. The dimensions of the cylinder used in the present work were 4 1/2″ outside diameter, 13″ long, inside diameter 17/32″ for the greater part of its length, with an enlargement to 3/4″ at the lower end for the reception of the manganin coil. The original inside diameter was 7/16″. The cylinder was prepared for use by hardening in oil and then subjecting to a pressure much in excess of that contemplated for the actual experiment. The seasoning pressure was over 30,000 kgm. Even under this high seasoning pressure the cylinder showed very little permanent change of internal dimensions, not stretching as much as 1/32.″ This is less than the amount of stretch which has been found for any other grade of steel. The

effectiveness of the treatment is shown furthermore in the fact that in over six months of continual use the inside has not stretched by so much as an additional 1/10000″. The hole was enlarged to a final size of 17/32″, instead of keeping it as small as possible, because of the difficulty of reaming out the hole so as to give a satisfactorily smooth surface after the seasoning process. The difficulty was occasioned by the hardness of the steel, and several attempts were necessary before the desired result was produced.

The pressure measuring coil was the same as that used in the last part of the work on ice VI. The construction of the insulating plug was also the same as that used there. During the course of the work it was necessary to take this plug apart several timess, because water had reached the mica washers, and once or twice the mica washers themselves have given way. These mica washers are the weakest part of the entire apparatus as at present used, since they gradually disintegrate and fail by shear after prolonged use, but it is a matter of only a few hours to replace them. Every time after the insulating plug has been freshly set up it has been tested for insulation resistance, both during application of pressure and after release. The resistance was in all cases as high as several hundred megohms, the limit of the measuring devise. The steel of the insulating plug has also failed once or twice by the "pinching-off effect" [6] after long use. This also is an easy matter to repair. Failure of this type is attended with some danger, however, because of the violence of the explosion with which the ruptured plug is expelled. The surest way of avoiding this danger is to so mount the apparatus that the plug points at the floor or other indestructible object.

The hydraulic press, the method of measuring the displacement of the piston, and the details of the packing of the moving piston, were the same as that used in the former paper.

In the use of the apparatus to determine compressibility there is one serious error which did not enter into its use in the determination of the change of volume during change of state, namely the correction for the distortion of the cylinder in which the piston moves. At low pressure the correction is relatively unimportant, and may be computed from the theory of elasticity, if one is willing to assume that the theory is sufficiently accurate for this type of stress. But at higher pressures the correction becomes more important, increasing in percentage value directly with the pressure, and is almost certainly

[6] Bridgman, Phil. Mag., **24**, 63–79 (1912).

not calculable by the theory of elasticity, because of the entrance of such effects as hysteresis. To determine the correction an auxiliary set of experiments is necessary. Evidently if the true value of the compressibility of some one substance were sufficiently well known, then the apparent compressibility as determined by this method would give the correction for the distortion of the cylinder. No such compressibilities are known with any high percentage accuracy, but this is not necessary, provided only that the uncertainty in the standard compressibility is small in comparison with the distortion of the vessel. The substance which most readily suggests itself because of its small compressibility is steel, but this is a solid, whereas the method is applicable directly only to liquids, so that some modification of the procedure is necessary. Such a modification readily suggests itself, and has been used by the author in the previous determinations of the thermal dilatation of water at temperatures below 0°, and has also been used by Parsons and Cook. The modification is to replace part of the liquid under investigation by a steel cylinder, and determine the compressibility of the liquid and the steel together. The difference of two determinations, the one for the liquid alone, the other for the liquid and the steel, gives a value for the difference of compressibility between the liquid and the steel from which the effect of the distortion of the vessel has been almost entirely eliminated. Furthermore, the compressibility of the steel is so small in comparison with that of the liquid that the slight uncertainty in the value for the steel is of no account, so that the compressibility of the liquid is given directly.

The application of this method would demand, then, that the interior of the cylinder be filled first with water and the apparent compressibility determined, and then part of the water replaced by steel and the apparent compressibility determined again. But this demands that the coil of manganin with which the pressure is to be measured come directly in contact with the water, which evidently cannot be allowed because of the short circuiting produced by the water. It seemed to be necessary, then, to devise some sort of protection for the coil, which should not occupy so much volume as to introduce a serious correction, and which should at the same time transmit the pressure readily to the innermost parts of the coil. Considerable time was spent in trying to devise such a protection. The scheme adopted was to surround the coil with a small mass of vaseline enclosed in a flexible sac, formed from the finger of a silk glove, and rendered impervious to water by painting it over with several coats of the col-

lodion of surgeons. This sac was tied with silk thread directly over the end of the insulating plug. It was proved by trial that the vaseline did not become so viscous under pressure as to refuse to transmit the pressure with sufficient freedom, but the arrangement did not prove itself as trustworthy as was to be desired. The collodion might leak after several applications of pressure, which made it necessary to reassemble the insulating plug and redetermine the elastic constants of the apparatus, because the distortion included in the plug itself was sufficient to introduce appreciable error. The device probably could have been made usable with a little more effort, but it would always have been more or less unsatisfactory, and would have been applicable only to those liquids which do not attack the collodion, whereas most of the organic liquids which it was desired to use in the future do so attack the collodion. The attempt to protect the coil was abandoned after a month's work, therefore, and the method replaced by another, which at first sight introduced additional complications, but which is really just as simple as the first, and has the advantage of being applicable with only slight modifications to the investigation of other liquids.

The modified method used two liquids in every determination, one beside the one whose compressibility is to be measured. The water under investigation is placed in a thin shell of steel fitting the inside of the cylinder. This shell, when in position in the cylinder, is surrounded on all sides and above and below by kerosene, which below transmits pressure to the manganin coil, and above reaches to the moving piston with which pressure is produced. In the auxiliary experiment to eliminate the effect of the distortion of the cylinder, the shell with water is replaced by a solid cylinder of steel, and the quantity of kerosene remains the same as before. The motion of the piston due to the change of volume of the kerosene remains the same in the two experiments, therefore, and the difference of readings of the two sets gives directly the difference of compressibility between the water and the steel. The disadvantage of the method is that it is not possible to use so large quantities of water as in the former method, because the steel shell containing the water remains invariable in length under pressure, and enough kerosene must be introduced originally to take up the change of volume of the water in this shell as well as the distortion of the other parts of the apparatus. The reduction in the quantity of water under experiment is not greater than 30%, however, and the other advantages more than outweigh this comparatively small loss of accuracy.

The procedure in using the apparatus in this finally modified form is as follows. The manganin coil is first screwed into the lower part of the cylinder. The rubber washer used to make this plug tight is one cut with a standard set of cutters, so that all the washers used for this purpose are always the same in size. This insures that the distortion due to the compression of the washers shall always be the same. The steel shell with the water in it is next introduced from above. The quantity of water is previously determined by weighing. It is desirable not to fill the shell to closer than 1/4″ of the top, experience having shown that otherwise water is likely to spill out and find its way to the manganin coil. The kerosene is next introduced into the cylinder from above. To ensure entire filling of all parts of the apparatus and the exclusion of air, only part of the kerosene is at first poured in, the air is then exhausted by attaching the mouth of the cylinder to an air pump, or simply by exhausting with the lungs, and then the remainder of the kerosene poured in. The amount of kerosene is determined by weighing the dish from which it is poured before and after filling. Because of the wetting of the dish by the kerosene it is not always possible to obtain exactly the amount of kerosene desired each time, but the variation is seldom over 0.02 gm., and the very slight effect of this discrepancy may be corrected for, as will be described later. Finally the movable plug is introduced into the top of the cylinder, taking particular pains not to allow any of the kerosene to escape in the process. Here again the rubber washer used has been cut with standard cutters, so that the amount of rubber used here is also the same in all the experiments. The cylinder is then placed in the thermostat, and the zero of the manganin coil read at the temperature of the room. The thermostat is then adjusted for the desired temperature and the cylinder seasoned for the run by the application of pressure.

A preliminary seasoning is necessary because of the hysteresis shown by the cylinder, and this hysteresis is shown with respect to both pressure and temperature. Many of the early results were somewhat in error because the necessity of this seasoning for temperature as well as for pressure was not clearly recognized. The method of seasoning to be adopted depends on the kind of data which it is desired to obtain from the run, whether the compressibility at constant temperature or the thermal dilatation at constant pressure. If it is desired to determine the isothermal compressibility, the seasoning consists simply in raising the pressure through the entire range and releasing several times. It was found by experiment that three

such preliminary excursions were sufficient; after this the cylinder settles down into a state in which the normal hysteresis cycles are retraced with perfect regularity. Of course it is necessary to make the compressibility determinations immediately after this seasoning, as the effect gradually disappears with time. The time occupied in making the final readings to 12,000 kgm. and back with increasing and decreasing pressure, making in all 20 readings, might vary from two to three hours. After every change of pressure it was necessary to wait for the temperature effect of compression to disappear; this time was from 5 to 7 minutes.

If the thermal dilatation under constant mean pressure is to be determined, the seasoning consists simply in taking the cylinder once through the temperature range contemplated as well as through the pressure range. A word of description as to the general procedure in determining the thermal dilatation at constant mean pressure will not be out of place. The general plan is to change the temperature while the piston is kept invariable in position, and therefore while the volume is also approximately constant. The rise of temperature produces a rise of pressure, so that after the rise of temperature it is necessary to bring the pressure back to the former value by withdrawing the piston if the change of temperature has been an increase, or advancing it if the change of temperature has been a decrease. The amount by which the piston is withdrawn, as also the new final pressure, is noted. The temperature is then changed again, and the same set of readings made again. Thus every observation at any given temperature involves two readings of the position of the piston and the corresponding pressure. The slight change of pressure during the changes of temperature carries with it hysteresis effects, which it is necessary to avoid by previous seasoning, exactly as for pressure changes over a wider range. Two processes of seasoning are necessary for temperature, therefore, one a larger one for the entire temperature range, and another smaller one for the slight changes of pressure incident to the changes of temperature. This second seasoning is made after the first more extensive seasoning simply by running the pressure back and forth several times through the small range of pressure to be met with during the temperature changes. This small range was determined by preliminary experiment.

In the actual calculation of the results there are a number of corrections to be applied. These will now be discussed in detail separately. In the first place the temperature coefficient of the manganin coil has to be determined with particular care. This is

because the pressure changes brought about by changes of temperature during the determinations of the thermal dilatation are comparatively slight, so that any change of the pressure coefficient of the coil brought about by the change of temperature appears in the result greatly magnified. Thus for the sake of example, we will suppose that a change of temperature of 20° produces a change of pressure of 400 kgm. at 10,000 kgm. total pressure. This figure is a fair average of the results to be met with in practice. If now the pressure coefficient of the coil is changed by 1% by this same rise of temperature, the pressure will thereby appear to have risen 500 kgm. instead of the actual 400, introducing an error of 25% for a change in the constant of the coil of only 1%. In addition to the effect of the temperature coefficient of the coil, there is an effect due to the change of the zero of the coil with temperature, but this change can be determined by observations of the temperature coefficient of the coil at atmospheric pressure and is easy to measure with the requisite accuracy.

The change in the pressure coefficient of the coil with temperature is more difficult to determine with the desired accuracy. It would not be possible to determine this by a direct calibration against the absolute gauge with which the mean value of the coefficient has been determined, for the reason that the absolute gauge itself is not accurate to better than 1/10%, and this would still leave a possible error in the thermal dilatation of 2.5%. To affect the desired calibration, some standard of pressure must be used which can be relied on to remain absolutely constant. Such a standard pressure is evidently afforded by the transition point of the liquid to the solid form of any convenient substance at some fixed temperature. In previous work the transition points of both water and mercury have been determined at various temperatures with an accuracy in the absolute pressure of 1/10%. To make the calibration it is only necessary to keep the pressure constant automatically at this known value by placing in communication with the chamber in which is the manganin coil to be calibrated another chamber in which are the liquid and solid forms of the substance whose transition temperature and pressure are known. This second chamber is to be kept at constant temperature accurately enough so that slight changes in this temperature will not produce changes of more than the allowed amount in the transition pressure. For this purpose the most convenient fixed temperature seems to be that of melting ice at atmospheric pressure, and the most convenient substance to use mercury, because of the sharpness of the freezing, and the ease with which it can be obtained pure.

The actual arrangements in making this calibration for the temperature coefficient of the pressure coefficient of the coil were as follows. The upper cylinder of the hydraulic press in which pressure was produced contained in addition to the moving plunger a steel shell in which was as large a quantity of mercury as convenient, about 150 gm. This upper cylinder as well as the entire lower part of the press was surrounded by a tank containing ice and water, by which the temperature of the mercury could be kept continuously and accurately at 0°. A heavy nickel steel tube led out of the lower end of the upper cylinder through the bottom of the tank, and connected with the lower cylinder in which was the manganin coil under examination. This lower cylinder was placed in an oil bath with thermostatic regulation, by which the temperature could be set at and retained at any desired value. The experimental procedure was as follows. The temperature of the lower bath was set at any desired value, and the pressure increased until the freezing point of mercury at 0° was slightly passed. The mercury then froze with decrease of volume, thus bringing the pressure back to the known equilibrium value at 0°. After equilibrium had been reached, the resistance of the manganin coil was read. The pressure was then lowered slightly by withdrawing the piston. This was followed by automatic restoration of the equilibrium pressure, brought about by melting of the frozen mercury with increase of volume. The transition point was always so sharp that no difference could be detected in the equilibrium pressure whether approached from above or below. The temperature in the lower cylinder containing the manganin was then changed to another desired value. This change of temperature, if it were an increase, would naturally carry with it a rise of pressure, but the pressure is then automatically lowered by the freezing of the mercury. After a steady state is reached, the new value of the manganin resistance is read, and then the pressure lowered again by slightly withdrawing the piston, and the value of the resistance noted again after the equilibrium conditions have been restored from below. In this way the coil can be calibrated over the entire temperature range contemplated for the experiments. Of course this calibration is good only for one fixed pressure, but in view of the proved linearity of the pressure-resistance relation within $1/10\%$ from 0° to 50°, it seemed safe to let the calibration go at this one determination, particularly since no effect could be found.

The calibration of the manganin was carried out at five temperatures; 25°, 45°, 65°, 85° and 110°. No appreciable change of the

coefficient could be found for the four lower temperatures, but between 85° and 110° there is a very perceptible change of 1%. But since the range of temperature of the actual experiment did reach over 80°, no correction was applied to the observations for this effect. It is to be noticed that this result is valid only for this one coil, since previous work, both by Lisell [7] and by the author, have shown that different pieces from the same spool of wire may show slight variations in the temperature coefficient, which is sometimes positive and sometimes negative.

In addition to this special calibration for slight relative changes in the pressure coefficient with temperature, the absolute value of the pressure coefficient has been checked from time to time during the course of the experiments. This could be done conveniently with the apparatus as used for the compressibility determinations by determining the transition point of ice VI, or of mercury at known temperatures. These calibrations have shown no change whatever in the pressure constant of the coil.

It has already been stated that the actual measurements involve two sets of readings, one with the apparatus filled with water, kerosene and a small amount of bessemer steel, and a second set with additional steel replacing the water. By subtracting the piston displacement at any given pressure for these two sets of experiments a value is obtained which gives approximately the piston displacement for the water alone, and from which the effect of the distortion of the vessel has in large measure been eliminated. But a moment's consideration will show that the effect of distortion has not been entirely eliminated, and it is necessary to apply a correction for the slight residual effect. The correction comes because of the fact that the position of the piston at corresponding pressures is not the same in the two sets of experiments, so that the subtraction leaves still uncorrected the distortion due to the part of the cylinder exposed to pressure in the one set of experiments and not so exposed in the other. This correction cannot be determined directly, and the only way seems to be to calculate it by the ordinary theory of elasticity, taking for the constant of the steel the values under ordinary conditions, which are known not to vary much even for the most different varieties of steel. There is undoubtedly some error in the correction as so determined, but the total value of the correction is at best small, and any such error is relatively unimportant.

[7] Lisell, Om Tryckets Inflytande på det Elektriska Ledingsmotståndet hos Metaller samt en ny Metod att Mäta Höga Tryck (Diss. Upsala, 1903).

The compressibility of the steel replacing the water also evidently enters as a correction factor. This compressibility is relatively slight, and it has been previously determined over a range of 10,000 kgm. The value of the compressibility of the steel also changes with the temperature, but this change has also been shown by direct experiment to be slight, so slight that it can be neglected. In the present work the value was assumed to be constant, independent of temperature and pressure, having the value 58×10^{-8} per kgm. per sq. cm.

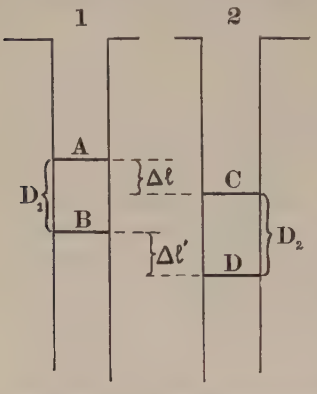

FIGURE 1. Diagram showing the position of the piston. To go with the computations for the corrections to be applied to the compressibility.

There is also a correction to be applied for the compressibility of the kerosene, if the amount does not happen to be the same in the two sets of experiments, and it was seldom that the amount was exactly the same. The variation was very small, however, and the correction is easy to apply if the compressibility of the kerosene itself is known. This was determined with sufficient accuracy for the purpose by an independent set of experiments, exactly the same in principle as those for determining the compressibility of water. The results of these independent experiments are given at the end of the paper.

The following formulas were used in making the corrections, and include all the corrections mentioned qualitatively above. Figure 1 shows the position of the piston at different times in the course of the experiment. The left hand part of the diagram (denoted by the suffix 1) is for the cylinder when it is filled with kerosene and bessemer steel only, and the right hand part (denoted by the suffix 2) is for the cylinder when it contains water, kerosene, and bessemer steel. A and C are the positions of the piston at the arbitrary zero of pressure in these two sets of experiments (this arbitrary zero was usually taken in the neighborhood of 2000 kgm. and will be denoted by p), and B and D indicate the position at some higher pressure, the same in the two sets, which will be denoted by p'. We now write down the expressions for the total volume of the cylinder beneath the piston.

$$\text{At A, } V_1 = V_{1k} + V_{1s}$$
$$\text{At B, } V_1' = V_{1k}' + V_{1s}'$$
$$\text{At C, } V_2 = V_{2k} + V_{2\,H_2O} + V_{2s}$$
$$\text{At D, } V_2' = V_{2k}' + V_{2'\,H_2O} + V_{2s}'$$

where the suffixes K, H_2O, or S indicate that the volume is for the kerosene, the water, or the steel respectively.

Subtracting the equations above from each other, we obtain

$$(V_1 - V_2) - (V_1' - V_2') = (V_{1k} - V_{1k}') - (V_{2k} - V_{2k}') - (V_{2\,H_2O} - V_{2'\,H_2O}) + (V_{1s} - V_{1s}') - (V_{2s} - V_{2s}').$$

We now denote by Δl the difference of displacements at the two positions A and C, and by $\Delta l'$ the corresponding difference at the positions B and D. We now assume that V_1 and V_2 differ only by the volume of the cylinder of length Δl, and similarly V_1' and V_2' differ only by the cylinder of length $\Delta l'$. This assumption is justified if only the positions of the pistons at A and C are so far removed from the end of the cylinder that the end effects in the distortion of the interior are the same in the two cases. This condition has been shown by the theory to be satisfied when the distance is two or three diameters, as it always was in these experiments. Hence we may write,

$$V_1 - V_2 = s_0 (1 + \alpha p) \Delta l$$
$$V_1' - V_2' = s_0 (1 + \alpha p') \Delta l',$$

where s_0 is the initial section of the cylinder at atmospheric pressure, and α is the factor of proportionality by which this is changed with pressure. Now if we call the displacement form A to B, D_1 and from C to D, D_2, then

$$D_2 + \Delta l = D_1 + \Delta l'$$

and the above equation may be thrown into the form

$$V_1 - V_2 - (V_1' - V_2') = -s_0(D_2 - D_1)(1 + \alpha p') + s_0 \Delta l \alpha (p - p')$$

We now make use of the fact that the total change of volume of any substance under pressure is proportional to its mass. If Δv (positive for a decrease) is taken as the change of volume of 1 gm. between p and p', then,

$$V_{1k} - V_{1k}' - (V_{2k} - V_{2k}') = \Delta v_k (m_{1k} - m_{2k})$$
$$V_{2\,H_2O} - V_{2'\,H_2O} = \Delta v_{H_2O}\, m_{H_2O}$$
$$(V_{1s} - V_{1s}') - (V_{2s} - V_{2s}') = \Delta v_s (m_{1s} - m_{2s})$$

This enables us to solve the equations for the compressibility of the water and the kerosene, giving,

$$\Delta v_{H_2O} = \frac{1}{m_{H_2O}}\{s_0 (D_2 - D_1)(1 + \alpha p') - s_0 \Delta l a (p - p') + \Delta v_k (m_{1k} - m_{2k}) + \Delta v_s (m_{1s} - m_{2s})\}$$

and for the kerosene, when the two runs are both made with kerosene, as in determining the data for kerosene given at the end of the paper,

$$\Delta v_k = \frac{1}{m_{2k} - m_{1k}}\{s_0 (D_2 - D_1)(1 + \alpha p') - s_0 \Delta l a (p - p') - \Delta v_s (m_{2s} - m_{1s})\}$$

The considerations so far apply only to the measurement of compressibility at constant temperature. The thermal dilatation is determined in the same way as the compressibility from the difference of the thermal dilatation as given by two sets of experiments, one with the water replaced by steel. The piston displacement is not the same at corresponding pressures here, either, and a correction is to be applied for the thermal dilatation of the part of the cylinder which is exposed to pressure in the one experiment and not so exposed in the other. But this portion of the cylinder to which the correction is to be applied was seldom more than 1″ in length, and the correction for this amount of steel is negligible in comparison with the thermal dilatation of the total quantity of water. There is also a correction to be applied for the dilatation of the steel replacing the water, and this correction is small but not negligible. It was assumed that the dilatation of the steel remains independent of the pressure over the pressure range used, and the value for ordinary mild steels at atmospheric pressure was employed. This value is 0.000039 for the cubic expansion per degree Centigrade.

The corrections to the measurements of the thermal dilatation are not so serious or so important as those for the compressibility, since the total effect is much smaller and most of the corrections become negligible. The method of determining the thermal dilatation has already been explained to be that of observing the change of pressure brought about at constant volume by a known change of temperature. From this the change of volume with temperature at constant pressure can be immediately determined if the slope of the p-v curve at that point is known, for $\left(\frac{\partial v}{\partial \tau}\right)_p = -\left(\frac{\partial v}{\partial p}\right)_\tau \left(\frac{\partial p}{\partial \tau}\right)_v$. $\left(\frac{\partial v}{\partial p}\right)_\tau$ is evi-

dently given directly from the curves for compressibility at constant temperature. The slope of this curve changes somewhat with the temperature, so that a correction should be applied for this, but the change is so slight at the higher pressures that for this purpose the compressibility can be assumed constant. At the lower pressures, below 2500 kgm., the change cannot be neglected, and another method of computation must be applied.

The thermal dilatation at low pressures was determined by taking directly the difference between the isothermals traced out at different temperatures. This method is not applicable at high pressures because the irregularities of isothermals traced at different times is sufficient to make their difference an inaccurate measure of the slight change of volume with temperature, but at the low pressures, the errors introduced by hysteresis and other irregular action of the steel cylinder are so slight that the method may be used directly to give the value of the compressibility, and by taking the differences, the value of the thermal dilatation. In fact it would seem that the method would be applicable with slight modifications to the determination of the compressibility of a great variety of substances at low pressures, and it is very much more rapid than the methods hitherto used.

A special setting up of the apparatus was necessary for the experiments at low pressures, because in order to be able to reach low pressure on release of pressure it is necessary that the friction in the movable plug be not too high, and if the pressure has once been run to so high a value as to upset the plug, the friction becomes so great as not to permit release of pressure to much below 1500 kgm. For these experiments, then, the plug was made initially a push fit for the hole, by making it about 0.0015″ smaller than when used for the higher pressures, and in performing the experiment the pressure was never pushed beyond 2500 kgm. In other respects the experiments at low pressures were the same as those at higher pressures. It was not necessary to take quite so elaborate seasoning precautions at these low pressures, however.

With regard to the amount of hysteresis or elastic after-effects to be met in the experiments, the difference of the displacment with increasing or decreasing pressure usually amounted at the middle of the range to 0.03 in. This amount was very uniformly consistent, indicating that the cylinder had really settled down to a steady behavior. The piston always returned to the starting point to within the limits of accuracy of reading, indicating that there was no leak or permanent set, or wearing of the packing in appreciable amount.

Of course the experiments at low pressures showed very much less hysteresis, in fact it was so small as to be almost imperceptible. The effect of hysteresis was eliminated as far as possible by using for the displacement at any pressure the mean of the results with increasing and decreasing pressure. The hysteresis was so constant that it would probably have been sufficient to have used consistently the results either at increasing or decreasing pressure. The actual procedure has, therefore, the weight of two independent determinations. In the determinations of thermal dilatation, on the other hand, the hysteresis effects were so much smaller, that except for one run initially to show that there was no effect of this kind, the readings were always made either only with increase or only with decrease of temperature for any mean pressure, never with both increase and decrease.

The Data.

Three independent sets of experiments were performed to give the change of volume with temperature and pressure over the entire range; namely the isothermal compressibility at pressures over 2500 kgm., the isothermal compressibility and the thermal dilatation at pressures below 2500 kgm., and the thermal dilatation at pressures over 2500 kgm. This is the actual order of experiment, but for the purposes of presentation it will be better to use the natural order, proceeding from low to higher pressures.

Compressibility at Low Pressures.

The method with the present form of apparatus is not very sensitive at the low pressures, and not many measurements were made over this range. Two sets of determinations of compressibility were made, the first at 20°, 40°, 60°, and 80°, and the second at only 20° and 80°. Here, just as for the measurements at the higher pressures, there is always sufficient friction in the packing after the pressure has once been applied not to permit of close enough approach to the zero to make an extrapolation back to the zero justifiable. And if the extrapolation to the zero is to be made from the readings during first application of pressure, special effort has to be made to design the washers so as to avoid small initial distortions. For this reason only the second of the above sets could be used by extrapolation back to the zero of pressure. The readings of volume at 20° and 80° were corrected back to 40° from the thermal dilatation as determined by this same set of experiments, so that we have from the above two values for the

compressibility at 40° up to 2200 kgm. The first set of readings at five temperatures is consistent with this latter set above 1000 kgm., but at the lower pressures gives values for the compressibility which are doubtless too high. To find the best value for the change of volume at low pressures we now have three sets of data, those of the

TABLE I.

VOLUME OF WATER AT 40° AND LOW PRESSURES BY DIFFERENT METHODS.

Pressure, kgm. cm.^{2}	Change of Volume, cm.^{3}/gm.			
	Steel Piez.	Piston.	Amagat.	Fina Mean.
0	.0000	.0000	.0000	.0000
500	.0200	.0202	.0204	.0203
1000	.0368	.0377	.0378	.0376
1500	.0527	.0527	.0534	.0532
000	.0669	.0667	.0676	.0673

present determination, those of the previous work by the method of the steel piezometers, and the results of Amagat. The most probable value for the change of volume has been found by comparing these three sets of values. These values are given in Table I, as also the mean selected from them as the most probable value from the data at present in hand. In taking this mean, the greater weight has been given to the values of Amagat at the lower pressures, since his method of measurement was doubtless more accurate for the low pressures than the present method, which was intended only for high pressures, but at the upper end of the range in the neighborhood of 2000 kgm., more weight has been given to the present determinations. It is to be noticed that the mean value taken as final is lower than that found by Amagat. This divergence is in the same direction as that found by Parsons and Cook, who worked with a method like the present one. The deviation found by them from the results of Amagat is greater than that adopted here.

Dilatation at Low Pressures.

For the thermal dilatation at low pressures, two sets of determinations were made; one was the series of isotherms at four different temperatures already mentioned, and the second was by the method adopted for the higher pressures, namely variation of temperature at constant mean pressure. The method of calculation for this lower

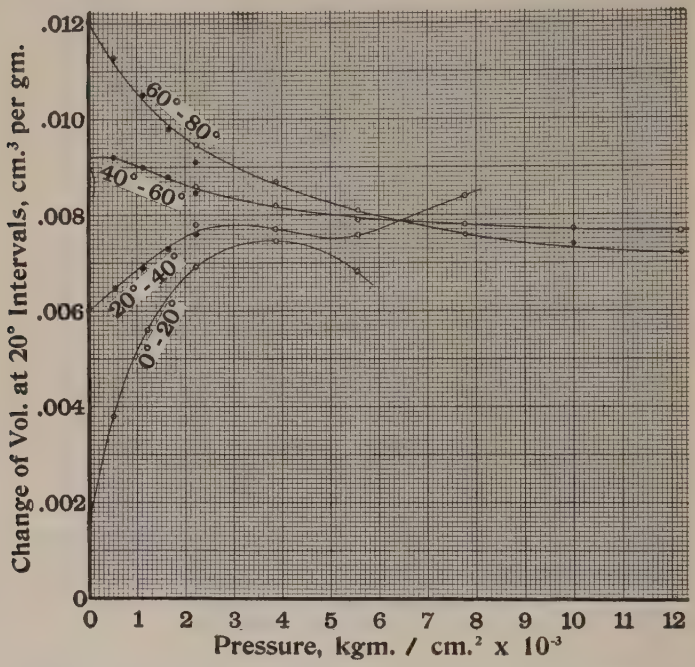

Figure 2. The change of volume of water for intervals of 20° plotted against pressure.

range was not the same as that employed for the higher pressures, as already explained, due to the fact that the slope of the isothermals is not sufficiently independent of temperature at the lower pressures. The method of computation adopted here was a graphical one, by plotting the observed volume and pressure points for the different temperatures and taking the difference between adjacent curves graphically. The temperatures at which the different determina-

tions were made were not exactly the even temperatures desired, namely 20°, 40°, and 60°, and 80°, but they were in all cases within a few tenths of a degree of these temperatures. The results were corrected to these even temperatures by assuming the mean variation with temperature over the whole temperature range to hold for the few tenths of a degree on either side. The final result given by the data is the total change of volume for an interval of 20°; from 20° to 40°, from 40° to 60°, and from 60° to 80°. The mean of the results of the two sets of experiments is shown with satisfactory accuracy in Figure 2, on which are plotted all the values obtained by the different methods. The results for the low pressures are shown in the full black circles. These values are seen to extrapolate, without forcing, to the values already found by other observers for atmospheric pressure, and they also make fairly good connections with the values found by the other method for the higher pressures. In view of this agreement it did not seem to be necessary to make further determinations of this quantity.

Compressibility at High Pressure.

The determinations of the isothermal compressibility at higher pressures extended over a considerable interval of time and are more numerous than any of the other determinations. In all, twelve determinations of this quantity were made, at five different temperatures. These determinations include those made during the early course of the experiment, when the attempt was being made to find the thermal dilatation directly from the difference of compressibility at different temperatures. A little work with the method showed that it was not sufficiently accurate for the purpose, but the results obtained then can be used to give the compressibility at the standard temperature, 40°, by applying the temperature correction found from the later more accurate results. The temperature of 40° was chosen as the standard because this is the lowest of the 20° intervals at which the water is liquid up to 12000 kgm.

The results of these twelve determinations, extending over a period of three months, are shown in Table II. The results as given are reduced to 40°, but the temperature at which the original measurements were made is given also in the table. Two of these sets of determinations differ considerably from the others, and were discarded in taking the mean, although as it happens one of these discarded sets is too high and the other too low, so that it makes very little difference

TABLE II.

RESULTS OF DIFFERENT DETERMINATIONS OF CHANGE OF VOLUME OF WATER AT 40°.

Pressure, kgm. cm.$^{-2}$	Change of Volume, cm.^{3}/gm.												
	Jan. 22–27.	Dec. 19–29.	Dec. 4–6.	Nov. 29-Dec. 1.	Nov. 27–28.	Nov. 24–25.	Nov. 9–10.	Nov. 8–9.	Nov. 6–8.	Nov. 3–4.	Nov. 2–3.	Nov. 1–2.	Final Mean.
2220	.0000	.0000	.0000	*.0000	.0000	.0000	.0000	*.0000	.0000	.0000	.0000	.0000	.0000
3330	.0255	.0256	.0266	.0268	.0255	.0262	.0257	.0243	.0260	.0253	.0256	.0250	.0257
4440	.0471	.0476	.0487	.0494	.0473	.0481	.0468	.0452	.0471	.0465	.0472	.0466	.0473
5550	.0656	.0666	.0675	.0687	.0660	.0670	.0652	.0635	.0650	.0648	.0658	.0652	.0659
6670	.0816	.0830	.0836	.0852	.0820	.0830	.0813	.0794	.0806	.0809	.0818	.0810	.0819
7780	.0956	.0974	.0979	.0999	.0962	.0970	.0956	.0937	.0947	.0953	.0961	.0952	.0961
8890	.1079	.1100	.1100	.1126	.1087	.1094	.1086	.1064	.1072	.1083	.1088	.1077	.1087
10000	.1190	.1211	.1213	.1238			.1201	.1178	.1186	.1198	.1201	.1189	.1199
11110	.1291	.1310	.1313	.1337			.1305	.1282	.1291	.1302	.1304	.1289	.1301
12220	.1386	.1398					.1412	.1377			.1413	.1408	.1403

* Discarded in taking mean.

in the final result whether they are included in the mean or not. For convenience in making the computations the pressure was taken in units given conveniently by the changes of the manganin resistance, the intervals of pressure corresponding to a displacement of the slider of the bridge wire of 5 cm.

TABLE III.

COMPARISON OF RESULTS BY TWO METHODS FOR CHANGE OF VOLUME OF WATER AT 20°.

Pressure, kgm. cm.^{2}	ΔV.		Pressure, kgm. cm.^{2}	ΔV.	
	Piston.	Piezometer.		Piston.	Piezometer.
2220	.0000	.0000	6670	.0814	.0821
3330	.0257	.0259	7780	.0954	.0964
4440	.0472	.0479	8890	.1078	.1105
5550	.0659	.0666	10000	.1190	.1229

These results, reduced to 20° are shown compared with the results of the previous determination in Table III. It is seen that the newer results are lower than the former ones, the difference being about 1%, except at the higher pressures, where the difference is greater. The agreement is perhaps not as close as could be desired, but at present there seems to be no way of choosing between the results. There is no consistent discrepancy, which would indicate a fundamental error in the present method, such as in the correction applied for the distortion of the steel cylinder, for example. If there were any such error it could be eliminated by so choosing the correction as to make the present results agree with the former ones. In the absence of any means of deciding between the two methods therefore, and since the results by the present method reach over a wider temperature and pressure range, and since also the method has been used much more extensively than the former one and with no greater discrepancy in the individual results, these present results have been accepted as the best ones. But it must be remembered that the absolute compressibility given here may be in error by as much as 1% at the higher pressures. This error, however, will not be found to invalidate any of the conclusions drawn from the data.

Dilatation at High Pressures.

The determinations of the thermal dilatation at the higher pressures were made on four occasions. The first two of these were preliminary, during which was discovered the necessity of seasoning for temperature as well as for pressure, and also the necessity for the secondary pressure seasoning over the small range of pressure accompanying the changes of temperature. These first two determinations, while confirming the results of the two later ones, were not given much weight in selecting the final value. The method of computation adopted in finding the thermal expansion from the data requires mention. At first an attempt was made to apply the same graphical method which has been already explained in its application to the determinations at the lower pressures. This method involves the drawing of a curve of the same general slope as the compressibility curve through the two points giving piston displacement against pressure at each temperature. But it was found that even after the seasoning for the small pressure range involved here, the points were too irregular to give good results by this method. The irregularities may be due to residual hysteresis, but are more probably due to slight irregularities brought about by the motion of the piston itself. These irregularities are too minute to have any effect on the compressibility determinations. The best way to avoid them is to utilize in the computations only those readings during which the piston remains stationary. This means that only the change of pressure accompanying a change of temperature is used in making the computations, the second reading at any temperature by which the pressure is brought back to the mean value being ignored. The change of volume at constant pressure for the given change of temperature is then computed from the known change of pressure at constant volume and the previously determined change of volume with pressure at constant temperature. In making this computation it is generally necessary to make two corrections; one to bring the temperature interval to the exact 20° desired for the final results, and the second to correct for the very slight change of measured piston displacement accompanying the change of temperature. This change of displacement is seldom over 0.003″. It is probably not due entirely to actual motion of the piston, but partly to temperature changes in the bars of the press which dip into the thermostat. That this method of computing the results is preferable to the graphical one previously mentioned is shown by the fact that this method gives very much

more uniform and consistent results when applied to the same set of data than the graphical method.

The method of computation adopted was first to calculate independently from the individual observations of each set of readings the thermal dilatation at six mean pressures between 2200 and 12,000 kgm. Then smooth curves were drawn through these points for each set of readings, the curves being spaced in the best way so as to give regular variations with both pressure and temperature. The values given by the smooth curves of each set of readings were then combined into the grand mean. In taking this grand mean, as already explained, almost the entire weight was given to the last two sets of readings. The agreement between the different sets was best at the higher temperatures, 60° to 80°, and about equally good between 20° and 40° and 40° and 60°. All four sets of curves, while not agreeing very well as to the numerical value of the coefficient, do agree as to the general character of the results, which are, perhaps, not quite what would be expected. The unexpected feature is the change in the sign of the temperature derivative of the dilatation at the higher pressures. At the low pressures the dilatation is greater at the higher temperatures, but at the higher pressures the thermal dilatation becomes less at the higher temperatures. This essential feature is verified on all four sets of curves. There are indications that it may be an essential characteristic of the behavior of any normal liquid at high pressures, and that it is not peculiar to water alone. This is shown by the work on kerosene, and is also indicated by the work at present being done on still other liquids. This will be taken up in greater detail later. The other feature not to be expected is the increase in the value of the thermal expansion between 20° and 40° at the higher pressures. It is to be distinctly expected that the thermal dilatation will decrease with rise of pressure, as indeed it does for all the other intervals of temperature, but this rise between 20° and 40° is shown by all the sets of determinations and seems to be an undoubted fact. It is probably connected with some new abnormality in the behavior of water at the higher pressures, which may be connected in some way with the appearance of the new variety of ice.

The values finally taken as the best values for the thermal dilatation are the mean of the results of the four determinations, much the greater weight being given, as already explained, to the two latter determinations. Figure 2 gives these results, as also those of the other methods at the lower pressures. The agreement of the two best determinations at the higher pressures is about 5% for the lower temperature

interval from 20° to 40°, 3% for the interval 40° to 60°, and 2% from 60° to 80°. The order of accuracy to be expected in these thermal measurements is not so great as that in the compressibility determinations, therefore, but perhaps the accuracy is as great as could be expected when one considers the smallness of the quantities involved, and the difficulty of making such measurements at high pressures. At any rate the absolute value of the coefficient cannot be very much in error. This is made probable by the agreement with the known values at atmospheric pressure. The accuracy is at least high enough to enable us to expect a fairly good quantitative description of the various thermodynamic quantities under high pressure, even those most sensitive to error. The calculation seems to be worth while carrying through in some detail, because such calculations seem never to have been undertaken for any substance, even for the low pressure range up to 3000 kgm., which is the range over which compressibility determinations have been previously made.

Discussion of Results.

The first necessity for a calculation of the various thermodynamic quantities is as accurate as possible a knowledge of the relation between pressure, temperature and volume over the entire pressure-temperature plane. It may be shown that this is sufficient to completely determine the thermodynamic behavior of the substance if in addition the behavior of the specific heat at constant pressure, for example, is known in its dependence on temperature at atmospheric pressure. This may be assumed to be known well enough for the present purpose. The first and the most important outcome of the present data is, therefore, the construction of a table giving pressure, volume, and temperature at sufficiently close intervals. In constructing this table the basis of computation was the compressibility as determined at 40°. This, together with the known value of the volume at 40° and atmospheric pressure, gave the volume as a function of the pressure down a line through the middle of the table at 40°. The values of the volume were tabulated for intervals of the pressure of 500 kgm., the values found graphically from smooth curves through the experimental points being so smoothed as to give smooth second differences. The values of the change of volume for intervals of 20° now were combined directly with these values to give the volume as a function of the pressure at 0°, 20°, 60°, and 80°. To find the intermediate values of the volume, smooth curves were drawn through

these five points at every constant pressure, and the intermediate values so chosen as to given smooth values for the second differences over the entire temperature range. The values for the points below zero, which are also given in the table, were taken directly from the previous work, the values for the dilatation found there being kept without modification, but the present value for the compressibility at 0° being used. The differences so introduced may be seen by comparison of the two tables to be only slight.

The table gives the volume to only four significant figures, since this is as many as the variations in the values of the compressibility would entitle one to, but in making the calculations of the thermal expansion it was necessary to keep three significant figures for the expansion, which would mean five figures in the table.

The thermal dilatation per degree rise of temperature was determined from the values used in the construction of the table for the differences of volume at 5° intervals by dividing by 5, and using the result as the thermal expansion at the mean temperature. The values of the total change of volume for five degree intervals had been smoothed so as to give smooth second differences, so that the dilatation as found in this way was smooth also with respect to the second differences, and could be used directly to give the second temperature derivative of the volume at constant pressure.

The difference of thermal dilatation at different temperatures can evidently be combined with the known compressibility at 40° to give the compressibility as a function of the temperature.

These several quantities so determined; the compressibility, the thermal expansion, and the second temperature derivative of the volume, in their dependence on temperature and pressure, are the basis of most of the calculations of the quantities of thermodynamic interest to be given presently. The accuracy of most of these quantites is not so high but that they can be shown as well in figures as in tables, and this manner of presenting them has been chosen as giving the most ready general survey of the facts.

The tables and figures follow. The results are given simply for themselves, without much comment, except to call attention to the unexpected features, or those properties which seem to be peculiarly characteristic of high pressures. It would not be safe to generalize from the behavior of this one liquid, abnormal at low pressures, to the general behavior to be expected for any liquid for high pressures and the bearing on a possible theory of liquids. Such a general treatment must be reserved for another paper, when the data for more liquids are in hand.

TABLE IV.

Volume of Water as a Function of Pressure and Temperature.

Pressure. kgm. / cm.	—20°	—15°	—10°	—5°	0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°	55°	60°	65°	70°	75°	80°
0			1.0017	1.0006	1.0000	0.9999	1.0001	1.0007	1.0016	1.0028	0.0041	1.0057	1.0076	1.0096	1.0118	1.0143	1.0168	1.0195	1.0224	1.0255	1.0287
500			.9795	.9778	.9771	.9778	.9786	.9796	.9808	.9821	.9837	.9854	.9873	.9894	.9916	.9940	.9965	.9992	1.0020	1.0049	1.0075
1000			.9598	.9584	.9578	.9589	.9602	.9616	.9630	.9646	.9663	.9681	.9700	.9721	.9743	.9766	.9791	.9816	.9842	.9869	.9896
1500		.9404	.9416	.9407	.9410	.9424	.9439	.9454	.9471	.9488	.9506	.9525	.9544	.9564	.9586	.9599	.9632	.9657	.9682	.9707	.9732
2000	.9228	.9235	.9243	.9252	.9260	.9276	.9293	.9310	.9327	.9345	.9364	.9383	.9403	.9423	.9445	.9467	.9489	.9513	.9537	.9561	.9585
2500	.9085	.9094	.9104	.9117	.9133	.9150	.9167	.9185	.9203	.9221	.9220	.9259	.9279	.9299	.9320	.9341	.9363	.9386	.9409	.9433	.9457
3000	.8963	.8972	.8984	.8997	.9015	.9032	.9050	.9068	.9087	.9106	.9105	.9144	.9164	.9184	.9205	.9226	.9247	.9269	.9292	.9314	.9337
3500		.8864	.8876	.8888	.8907	.8924	.8943	.8961	.8979	.8998	.8997	.9036	.9056	.9076	.9096	.9117	.9138	.9160	.9182	.9204	.9226
4000		.8766	.8774	.8786	.8807	.8825	.8843	.8861	.8880	.8889	.8897	.8936	.8956	.8976	.8996	.9016	.9037	.9058	.9080	.9101	.9123
4500			.8684	.8695	.8717	.8734	.8751	.8770	.8788	.8807	.8805	.8844	.8864	.8884	.8904	.8924	.8945	.8965	.8966	.9008	.9028
5000			.8599	.8610	.8632	.8649	.8666	.8684	.8702	.8721	.8719	.8758	.8778	.8798	.8818	.8838	.8858	.8879	.8899	.8920	.8940
5500				.8537	.8554	.8569	.8585	.8603	.8621	.8640	.8639	.8678	.8698	.8718	.8737	.8757	.8777	.8798	.8818	.8838	.8858
6000				.8464	.8480	.8494	.8509	.8527	.8545	.8564	.8654	.8603	.8623	.8643	.8662	.8682	.8702	.8722	.8742	.8762	.8781
6500					.8409	.8423	.8438	.8454	.8473	.8492	.8493	.8532	.8552	.8572	.8591	.8611	.8631	.8650	.8670	.8689	.8709
7000							.8370	.8386	.8404	.8424	.8425	.8465	.8485	.8505	.8524	.8544	.8564	.8583	.8602	.8621	.8640
7500							.8305	.8321	.8338	.8360	.8361	.8401	.8421	.8441	.8460	.8480	.8499	.8519	.8538	.8557	.8575
8000								.8259	.8275	.8298	.8300	.8340	.8360	.8380	.8399	.8419	.8438	.8457	.8477	.8495	.8513
8500								.8200	.8216	.8240	.8262	.8283	.8303	.8323	.8342	.8361	.8381	.8400	.8419	.8437	.8455
9000									.8160	.8185	.8208	.8229	.8249	.8269	.8288	.8308	.8327	.8346	.8364	.8383	.8401
9500										.8133	.8156	.8178	.8198	.8218	.8237	.8256	.8275	.8294	.8313	.8331	.8349
0000										.8083	.8107	.8129	.8149	.8169	.8188	.8207	.8226	.8245	.8264	.8282	.8300
10500											.8060	.8082	.8102	.8122	.8141	.8160	.8179	.8198	.8216	.8235	.8252
11000												.8036	.8056	.8076	.8095	.8114	.8133	.8152	.8170	.8188	.8206
11500												.7991	.8011	.8031	.8050	.8069	.8088	.8107	.8125	.8143	.8160
12000													.7966	.7986	.8005	.8024	.8043	.8062	.8080	.8098	.8115
12500													.7922	.7942	.7961	.7980	.7999	.8017	.8036	.8054	.8071

In presenting the results, the quantities have been arranged in order of simplicity of the thermodynamic formulae, which is also the order of directness with which they are derived from the experimental data.

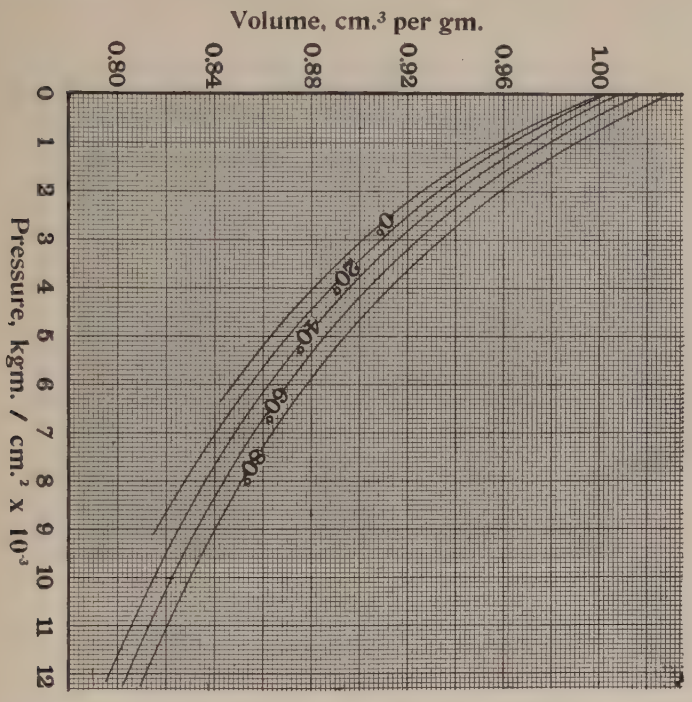

FIGURE 3. Isothermal lines for water, showing volume against pressure.

In Table IV are given the values of the volume for intervals of pressure of 500 kgm., and intervals of temperature of 5°. The table does not require comment. It was computed in the way already described. The values of the volume at intervals of temperature of 20° are shown as a function of the pressure in Fig. 3. The figure does not show the results as accurately as the table, but enables one to form a clearer mental picture of the nature of the results. The curves, on the scale of the figure, do not show any abnormalities to the eye, except in the neighborhood of the origin, where the well known negative expansion at 0° results in the curves drawing together.

There are various abnormalities besides those in the neighborhood of 0°, however, as will be shown by the other figures.

With regard to the compressibility there seems to be some variance of usage, so that it will be well to call attention to the fact that the quantity used throughout this paper in the sense of compressibility is

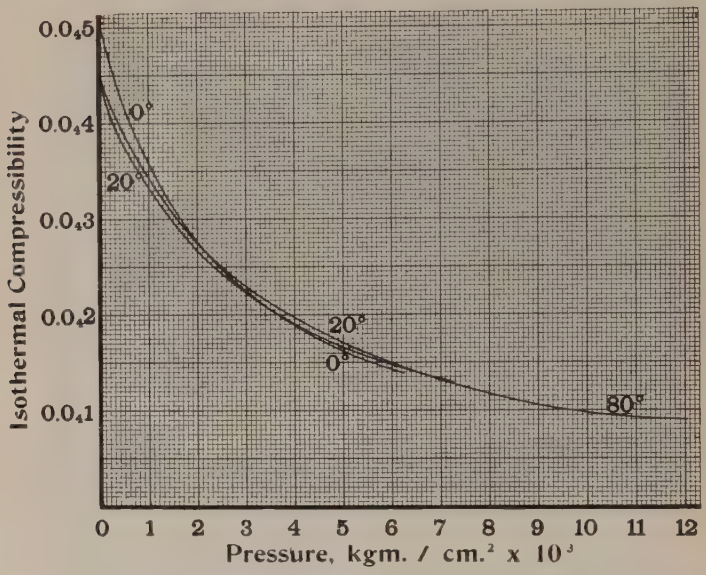

FIGURE 4. The isothermal compressibility of water, $\left(\frac{\partial v}{\partial p}\right)_t$ against pressure.

the derivative $\left(\frac{\partial v}{\partial p}\right)_t$. Sometimes the expression $\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_t$ is used in the same sense. Figure 4 shows the compressibility, that is, the analytic expression $\left(\frac{\partial v}{\partial p}\right)_t$, as a function of the pressure at 0°, 20°, and 80°. It would have made the figure too crowded to have tried to show the values for 40° and 60° also. The complete values for the five standard temperatures are shown in Table V separately, however. The figure shows the well known abnormality in the compressibility at the low pressures, namely a higher compressibility at the lower than at the higher temperatures. This abnormality disappears above 50°, and from here on the compressibility increases with rising temperature. The figure shows that at 80° the initial compressibility is higher than

at 20°, although it has not yet risen to the value at 0°. In addition to the abnormality at low pressures, the curve shows also a slight

TABLE V.

COMPRESSIBILITY OF H_2O.

Pressure, kgm./cm.²	$\left(\frac{\partial v}{\partial p}\right)_t$, cm.³/gm.				
	0°.	20°.	40°.	60°.	80°.
1	.0000	.0000	.0000	.0000	.0000
0	504	453	440	438	450
500	417	381	371	373	388
1000	360	336	328	332	346
1500	313	298	292	296	306
2000	276	267	263	267	274
3000	225	223	222	224	229
4000	189	191	191	193	198
5000	162	166	165	166	170
6000	143	148	146	147	149
7000		133	130	130	132
8000		121	117	117	119
9000			104	104	105
10000			096	096	097
11000			091	091	092
12000			089	089	090

abnormality at the higher pressures in the neighborhood of 6500 kgm. Here the compressibility at 20° rises and at the melting point of ice VI, it has become higher than the compressibility at 80°. The thermal dilatation shows abnormality in the same locality; it would seem to be

connected in some way with the appearance of the new variety of ice, but the exact connection cannot at present be stated.

The large change in the value of the compressibility brought about by pressure should be noticed, amounting at 12,000 kgm. to a decrease of five fold. Furthermore the rapid flattening of the curve at the higher pressures also should be commented on. The curve gives the appearance, for the pressure ranges used here, of becoming asymptotic to some value greater than zero. Of course this cannot really be the case for infinite pressures, for otherwise we should have the volume completely disappearing for some finite value of the pressure, but it may indicate the entrance of another effect at the higher pressures, which may persist in comparative constancy for a greater range of pressure than will ever be open to direct experiment, such an effect as the compressibility of the atom, for example. This possibility has been already mentioned and made plausible from the data of the preceding paper.

If instead of the compressibility as defined above, the quantity $\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_t$, which in this paper will be called the relative compressibility, is plotted, a curve of the same general character as that shown will be obtained.

The compressibility may also be plotted against a different argument than the pressure. For many purposes the pressure is perhaps not the most significant independent variable that might be chosen. This is because the external pressure is not a measure of what is happening inside of the liquid. We conceive a liquid as composed of molecules in a state of constant motion and of collision with each other, acted on also by attractive forces between each other. The effect of these attractive forces is to produce at the interior points a pressure which may be much higher than the external pressure. The external pressure is equal to the interior pressure diminished by the amount of the attractive pressure drawing the molecules to the interior at the exterior surface, where the attraction is an unbalanced action in one direction. The amount of the unbalanced pressure at the outside depends in a complicated way on the law of attraction between the molecules, on their mean distance apart in this surface layer, and on the distribution of velocities in this layer. The external pressure required to hold the liquid in equilibrium is, therefore, largely a surface phenomonon, and is connected in a complicated way with the state of affairs at inside points. A more significant independent variable, therefore, would be one involving only the condition of the

molecules on the average throughout the mass, and not one dependent on the surface layer. There are only a few such quantities depending on the state of the liquid at interior points. Any quantities involving in any way the constancy of pressure or of entropy, for example, do depend on the complicated action of the surface layer. One of the quantities which is independent of this surface layer, however, is the volume. In many theoretical considerations the use of the volume as an independent variable is known to produce simplifications.

If the volume, instead of the pressure is taken as the independent variable for the compressibility, curves are obtained of the same general appearance as when the pressure is used for the variable. The compressibility falls with decreasing volume, and the curvature is in the same direction as when the pressure is the independent variable. The same general characteristics are also shown if the relative compressibility instead of the compressibility is plotted against the volume. The two sets of curves, for the compressibility and the relative compressibility, do show one feature in common, however, different from the curves when the pressure is used as the variable. This is the fact that the compressibility is always lower for the same volume at the higher temperature. This is true throughout the entire range of volume used; there is no crossing of the curves indicating abnormalities, such as is the case when the pressure is used as the variable. This is what one would expect on the kinetic theory. A liquid, at two different temperatures but at invariable volume, differs only in the violence of the motion of its molecules. At the higher temperature, the kinetic pressure due to the motion is greater, and so the resistance offered to change of volume under a given increase of external pressure is greater when the temperature is higher.

Fig. 5 shows the thermal dilatation as a function of pressure at various temperatures. The thermal dilatation plotted in the figure is the expression $\left(\frac{\partial v}{\partial t}\right)_p$ instead of the expression $\frac{1}{v}\left(\frac{\partial v}{\partial t}\right)_p$, which is sometimes used as the dilatation. The usage adopted here for the dilatation is analagous to that explained above for the compressibility. The values listed in the figure were obtained from the table of volumes in the manner already described. The curve at 0° was obtained from the data of the previous paper for the low temperatures, but in that paper the mean value of the thermal expansion for the range 0°–20° was given, whereas here the instantaneous value at 0° is given instead. The substitution of the instantaneous for the mean dilatation produces no change in the general character of the curves, however.

The points at the higher temperatures were obtained from the data of this paper alone. There are two striking features that call for special comment. The first of these is the abnormal behavior of the curve for 20°. In the initial stages, the dilatation rises with increasing pressure, unlike normal liquids, but this merely indicates the return of water to the normal behavior to be expected at high pressures. At about 3500 kgm. the curve at 20° has reached a maximum and begins to descend with increasing pressure, as it does for the curve at 0°. But the descent continues for only a little way, and at 5500 kgm. the curve begins to rise again, indicating the entrance of a new abnor-

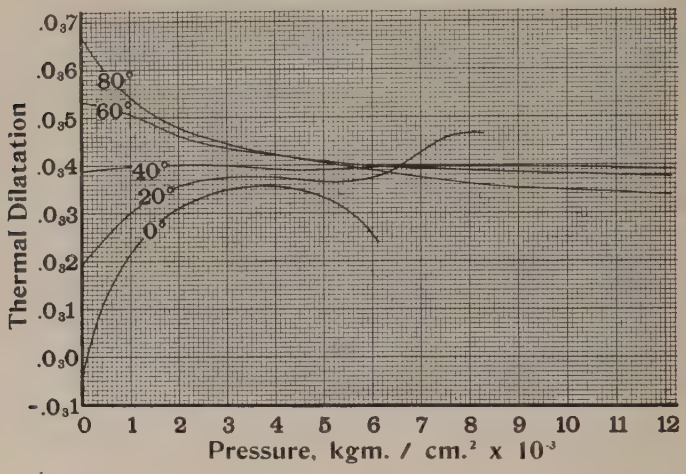

FIGURE 5. The dilatation of water, $\left(\frac{\partial v}{\partial t}\right)_p$, against pressure.

mality. The abnormality is not so striking or so great in amount as that in the neighborhood of 0° and atmospheric pressure. The abnormality at 20° continues for about 2500 kgm., up to 8000, where the curve is terminated by the entrance of the solid phase, but the direction of the curve has already begun to change, indicating that if it could be continued, this abnormality also would probably disappear at higher pressures. As to the question of experimental error here, there would seem to be no room for doubt as to the actual existence of this new abnormality, for it was shown by all four of the dilatation curves, even those taken before the method was got to running satis-

factorily, and in which the accuracy was not very high. The curves at the higher temperatures behave as one would be prepared to expect in the region of low pressures. The curve for 40° shows vestiges of the abnormal behavior at the low pressures, namely slight initial rise of dilatation with rising pressure, followed by a fall, but the curves at the higher temperatures, 60° and 80°, show the regular initial decrease with rising pressure shown by all normal liquids. But at higher pressures, the behavior of all three of these curves, for 40°, 60° and 80° is different from what might be expected. The unexpected feature consists in the crossing of the curves, all in the vicinity of the same pressure, 5500 kgm., so that at higher pressures the thermal dilatation at the higher temperatures is lower than it is at the lower temperatures. It has been already remarked that there are indications, both from the present work and from that of Amagat, that this may be the behavior for any normal liquid at sufficiently high pressures. The comparative constancy of the thermal dilatation at the higher pressures, is also a matter perhaps not to be expected. Thus the expansion at 40° remains nearly constant over the entire range of pressure, while the compressibility has in the same range dropped from 44 to 9. It was distinctly expected, before these measurements were taken, that the dilatation would show the greater variation with pressure, so that the effect of temperature on the volume would tend to disappear at the higher pressures, but such is not the case.

The relative thermal dilatation may be plotted against pressure, as was the relative compressibility. The curve shows no striking features. The curve plotting relative dilatation against volume has also been plotted, and this is the same in general character as the others. The slight differences consist in an accentuation of the abnormalities in the neighborhood of 5500 kgm., and the fact that at the lower volumes, that is at the higher pressures, the dilatation against volume increases with decreasing volume for 40° and 60°, but decreases for 80°.

These figures for the thermal dilatation and the compressibility complete those which are obtainable directly from the table. Other quantities of thermodynamic interest may be obtained by combining these, however. Perhaps the simplest of these quantities are those connected with the absorption of energy when the pressure is changed at constant temperature. The first of these is the actual mechanical work done by the external pressure in compressing the liquid at constant temperature. This of course is simply the expression

$W = \int p \left(\frac{\partial v}{\partial p}\right)_t dp$. It was obtained by a mechanical integration from curves similar to the volume curves of Figure 3, drawn on a larger scale. For this purpose the integrating machine owned by the mathematical Department of Harvard University was used. The

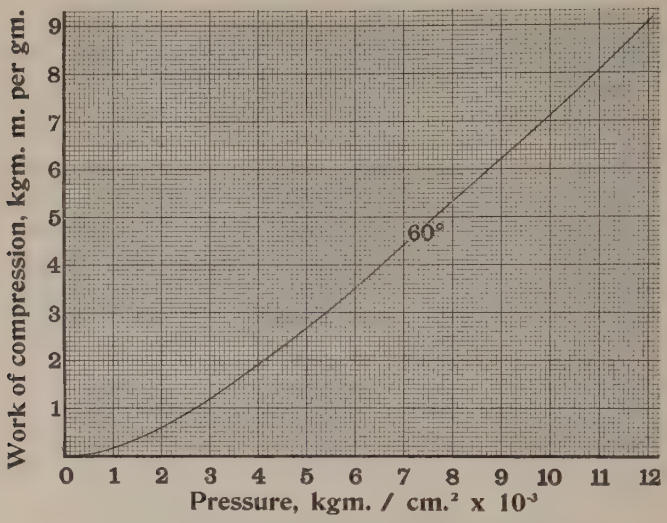

FIGURE 6. The mechanical work of compression at 60°.

actual value of the mechanical work at any pressure is of course dependent on the temperature, but since the variation is so slight that it would have been impossible to show it in the figure (see Figure 6), the work of compression is plotted for only the one temperature, 60°. Although the change of external work with temperature was too slight to show in the diagram, the change with temperature was nevertheless taken account of in making the calculations of the quantities depending on it to be described immediately. After the first 4000 kgm. it is seen that the curve becomes very approximately linear. The curve for a substance which retains the same compressibility unchanged over a wide pressure range, as steel for example, is a parabola, the work increasing directly as the square of the pressure. That this curve for water becomes linear, means that the compressibility decreases so fast with increasing pressure that the decrease in the yield

of the liquid for a given increment of pressure decreases almost at the same rate that the pressure itself increases.

The total heat given out during an isothermal compression may be derived from the formula $\left(\frac{\partial Q}{\partial p}\right)_\tau = -\tau\left(\frac{\partial v}{\partial \tau}\right)_p$. This quantity is shown in Figure 7. The figure does not call for especial comment. The

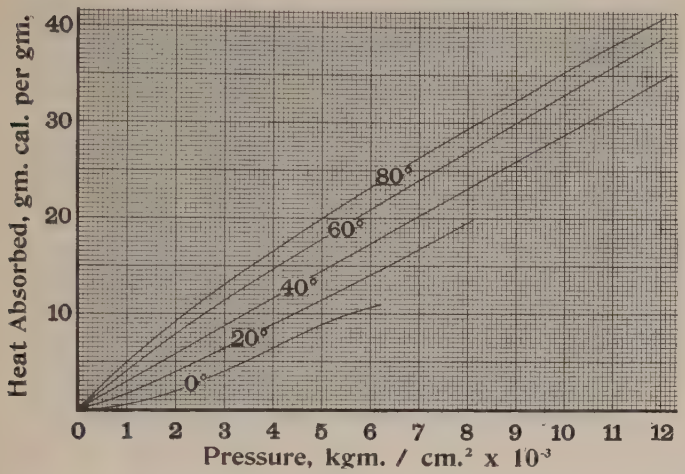

FIGURE 7. The heat given out by water during an isothermal compression.

rapid change in the direction of the isothermal lines in the vicinity of the origin due to the abnormal behavior at low temperatures and pressures is manifest from the figure, as also the slight abnormalities at the upper ends of the 0° and the 20° curves, already commented upon in other connections. Beyond 5000 kgm. the curves for all temperatures tend to become linear and parallel to each other.

These two quantities, the heat liberated in compression and the mechanical work, combine to give the change of internal energy along an isothermal, this change of energy being equal to the difference of the heat and the mechanical work. The change of energy so calculated is shown in Figure 8. The change is a decrease, which continues at all temperatures up to the highest pressures. In the previous paper a value of this quantity was given, confessedly inaccurate, since in the computation the mean thermal dilatation between 0° and 20° had been used instead of the actual dilatation at 0° or 20°. The

curve so obtained had the characteristics of the curve now given for 0°, but the maximum at the top was much more strongly accentuated than in the present figure. It was surmised in the previous paper that at high enough pressures the internal energy of all liquids would probably increase instead of decrease along an isothermal. This surmise seemed

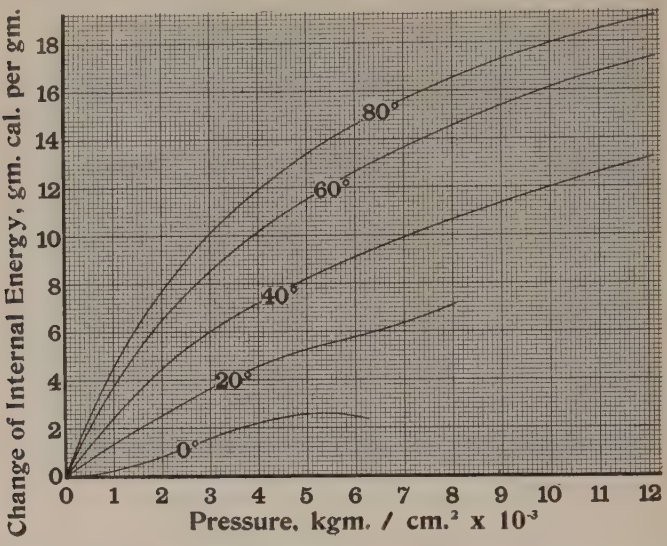

FIGURE 8. The decrease of internal energy of water during an isothermal compression.

plausible because one would expect that at high enough pressures the energy stored up as strain in the interior of the molecules in virtue of the extremely high pressures would more than counterbalance the work done by the attractive forces of the molecules themselves as they were brought closer together by the action of the pressure. This present figure shows that this is not the case, however, for the range of pressure reached here. The lower temperature, 0°, is the only one at which this reversal of the direction of the change of internal energy manifests itself, and this change, in comparison with the other curves, is now seen probably to be an effect of the other abnormalities shown at low pressures and temperatures. Nevertheless it would still seem as if at very high pressures the energy must increase instead of decrease along an isothermal, but the only indication of it from the present curves is in the direction of curvature, which is in the direction

to indicate the possibility of a maximum and a reversal of direction at higher pressures. The pressure for a maximum, however, if there is one, is much beyond the reach of any at present attainable. Within the pressure range of these measurements, the attraction between the molecules still remains the dominant feature, so that the work done by the attractive forces and liberated as heat much more than suffices to overbalance the mechanical work of compression.

The internal energy of a substance is one of those quantities which depend only on the properties of the mass of the substance at interior points and do not involve the action of the surface layer. Change of energy plotted against volume shows in the first place that the change of internal energy is much more nearly a linear function of the volume than it is of the pressure. The average slope of the isothermal lines of energy increases rapidly with rising temperature for the lower temperatures, but the two curves for 60° and 80° run nearly parallel to each other for their length. Abnormalities are shown at the upper ends of the 0°, 20° and the 40° curves, and the 0° curve shows the same maximum as it does when plotted against pressure. The origin, of course, for the curves at different temperatures does not coincide as it does for the same quantities when plotted against pressure.

One other quantity may be simply determined in terms of the compressibility and the thermal dilatation alone, the so-called pressure coefficient, that is, the change of pressure following a rise of temperature when the temperature is raised by 1° at constant volume. This quantity is given immediately in terms of the compressibility and the thermal dilatation by the well known formula,

$$\left(\frac{\partial p}{\partial \tau}\right)_v = -\left(\frac{\partial v}{\partial \tau}\right)_p \Big/ \left(\frac{\partial v}{\partial p}\right)_\tau .$$

It is shown plotted in Figure 9. The curves for 0° and 20° show anomalies, as is indicated by the unexpected direction of curvature. The other curves for the higher temperatures seem to be regular enough, though of course it cannot be told whether the course of these curves is the same as that which would be shown by a normal liquid or not. At the upper ends of the high temperature curves, the curvature is in such a direction that if they were continued far enough the pressure coefficient would decrease instead of increasing with rising pressure.

This quantity, the pressure coefficient, has been made the basis of theoretical speculation. It has been enunciated as a law, approximately true, by Ramsay and Shields, that the pressure coefficient

is a function of the volume only. This means that if the coefficient were plotted against volume instead of pressure the curves for all five temperatures would fall together. That this is not the case for water at high pressures is shown very distinctly in Figure 10. At the lower pressures and the larger volumes, the curves for the different tempera-

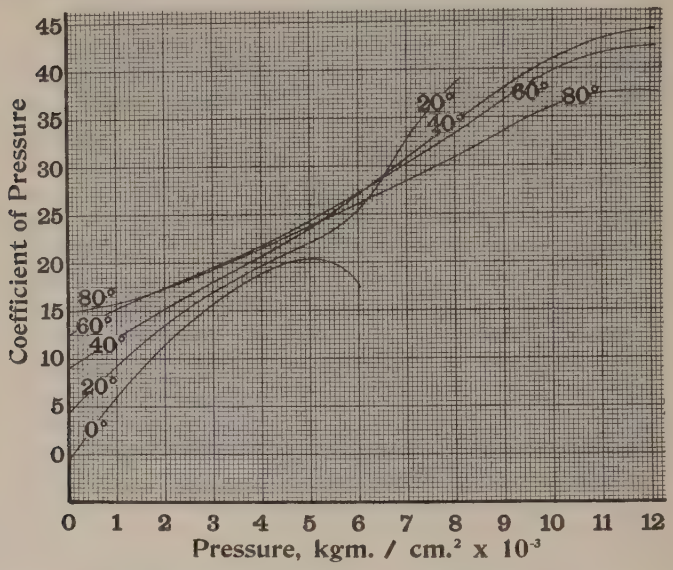

FIGURE 9. The pressure coefficient, that is the change of pressure accompanying a rise of temperature of one degree, as a function of the pressure.

tures are very widely separated. The abnormality on the curve at 0° in the neighborhood of the locality where the new variety of ice makes its appearance is very striking. At the higher pressures the curves do draw together, but they are not approaching coincidence, for they cross in the neighborhood of a volume of about 0.85. It does not seem likely that the entire failure of coincidence throughout the whole range of pressure can be due to abnormalities, since even at low pressures water is nearly normal at the higher temperatures, and certainly at the higher pressures and temperatures we have every reason to expect that its behavior is quite like that of other liquids.

This completes the list of quantities which can be deduced directly from the compressibility and the thermal dilatation. Other quanti-

ties of thermodynamic interest involve the specific heats, and these in turn involve the second temperature derivative of the volume.

The first of these quantities is the specific heat at constant pressure. This is given by the thermodynamic equation $\left(\frac{\partial C_p}{\partial p}\right)_\tau = -\tau\left(\frac{\partial^2 v}{\partial t^2}\right)_p$. It will be seen that only the derivative of the specific heat is given by the data as directly determined. In order to obtain the specific heat itself, the derivative, obtained from the tables in a manner already described, must be integrated. This integration was performed mechanically, in the same manner as the integration for the mechanical work of compression. The results are shown in Figure 11. The values for the specific heat as a function of temperature at atmospheric pressure were taken from the steam tables of Marks and Davis.[8] These values seem to be open to some slight question at the present time due to experimental work done by Bousfield [9] since the publication of the tables, but in any event the possible error is slight, too slight to be visible on the scale of the figure. The curves show the now expected abnormalities at 0° and 20°. The striking feature about the curves for the higher temperatures is the very rapid increase of the specific heat with rising temperature at the higher pressures. The specific heat at first decreases on all the curves except at 0°, but passes through a minimum, and then increases. The pressure of the minimum rapidly becomes less with rising temperature, and is situated at 6500 kgm. for 40°, 5500 kgm. for 60°, and at 1100 kgm. for 80°. At 80° the specific heat rises rapidly beyond the minimum, reaching the value 1.17 at 12000 kgm.

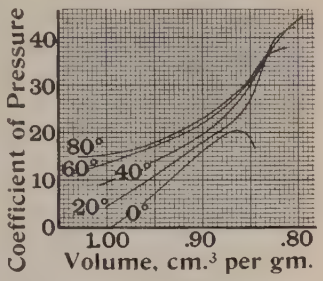

FIGURE 10. The pressure coefficient of water as a function of the volume.

Any valid characteristic equation should predict the behavior of the specific heat at high pressures as well as giving the volume in terms of pressure and temperature, since from the equation the second temperature derivative of the volume may be found. The equation of Tumlirz [10] has been mentioned in the preceding paper as giving perhaps as good agreement as any with the previously known facts over

8 Marks and Davis, Steam Tables. (Longmans, Green, and Co.)
9 W. R. and W. E. Bousfield, Trans. Roy. Soc. (A), **211**, 199–251 (1911).
10 Tumlirz, Sitzber. Wien, Bd. **68**, Abt. IIa (Feb., 1909), pp. 39.

a pressure range of 3000 kgm. This equation would predict a continuous diminution in the specific heat up to infinite pressures, the limiting value being very approximately 0.5. It was shown in the preceding paper that there is some new effect introduced at the high pressures which does not make itself felt at the low pressures, with the

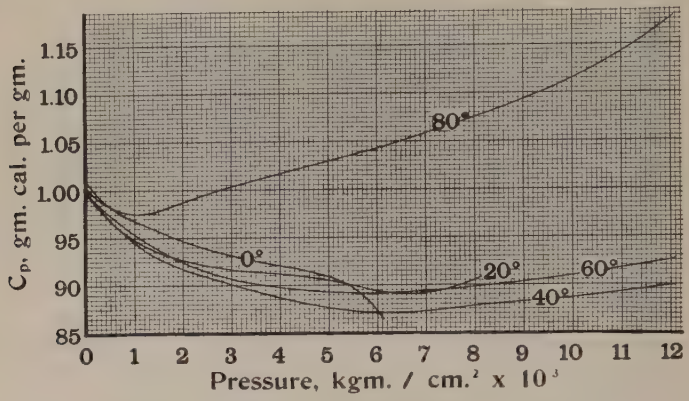

FIGURE 11. The specific heat at constant pressure of water as a function of the pressure.

result that an extrapolation to infinite pressures from the behavior for the first 3000 kgm. is not safe. This was shown in that paper by the behavior of the volume, which tended to decrease more rapidly at the high pressures than was predicted by the formula. The present data also show that there is a new effect at the high pressures, and indicate that the effect, whatever it is, is such as to have a much greater influence on the specific heats than on the volume itself.

The specific heat at constant volume may be found from the specific heat at constant pressure by means of the formula, $C_p - C_v = -\tau \frac{\left(\frac{\partial v}{\partial \tau}\right)_p^2}{\left(\frac{\partial v}{\partial p}\right)_\tau}$. This quantity, so calculated, is shown in Figure 12. The same abnormalities are shown at 0° and 20° as were shown in the curves for C_p. The curves for 40° and 60° decrease for nearly their entire lengths, although they are just beginning to rise at the very highest pressures, but the curve for 80° shows the same sharp turning point and the same rise through the greater part of its length as the curve

for C_p. This quantity, the specific heat at constant volume, has more theoretical significance than the other specific heat, since this represents the heat going into the rise of internal energy of the liquid when the temperature rises, and does not involve the work done against external pressure in expanding the liquid. The external work in-

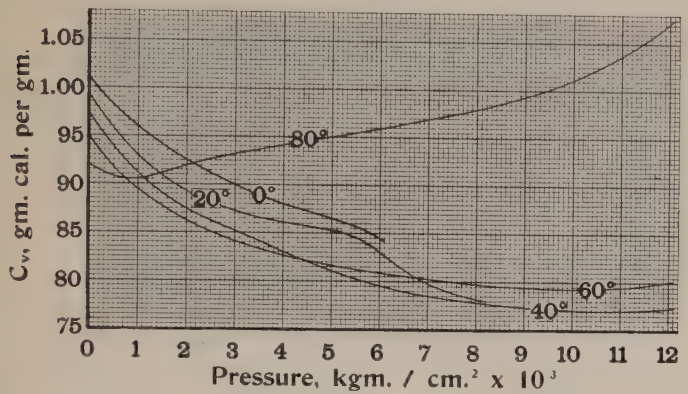

FIGURE 12. The specific heat at constant volume of water as a function of the pressure.

volves in a complicated and at present unknown way the action of the surface layer, while the specific heat at constant volume does not contain this surface effect. This specific heat is therefore one of the quantities mentioned in the beginning as having significance because it does not involve the unknown attractive forces between the molecules as displayed in the surface layer. In order to show this independence of the surface layer, of course C_v should be plotted against a variable not itself involving the action of the layer. It is evidently not adequate, therefore, to plot C_v against the pressure as as been done in Figure 12. C_v plotted against volume may be expected to show this independence of the action of the surface layer. It is shown so plotted in Figure 13. The figure is of the same general character as that in which it is plotted against pressure, but the separation of the curves for the different temperatures is greater, partly because the curves do not start from a common origin. The minimum on the curves for 40° and 60° comes at a lower pressure than it does in the former figure, and the upper end of the 80° curve is perhaps a trifle steeper at the upper end, but there are no essential differences. The entire behavior of the curves is not what one would

expect from the ordinary theoretical considerations, however. It is usually considered that when the volume of a substance is kept invariable all, or else a fixed fraction, of the heat put in during a rise of temperature goes toward increasing the kinetic energy of the molecules. This is because the temperature is supposed to be proportional

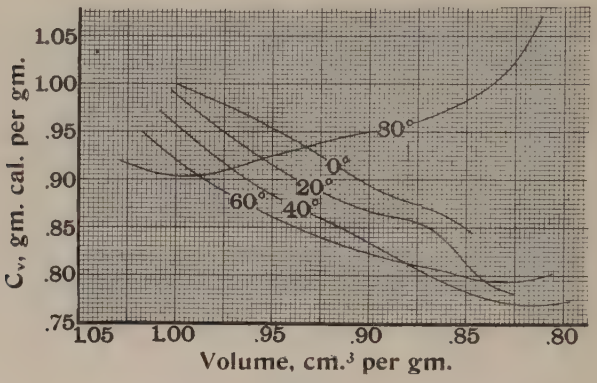

FIGURE 13. The specific heat at constant volume of water as a function of the volume.

to the energy of translation of the molecules, and therefore, because of the law of the equipartition of energy, to the total energy of the molecules. We should expect, therefore, that the input of energy required to raise the temperature by a specified amount would involve only the interval of temperature, and would be independent of the absolute value of the temperature and of the volume. The curves show most convincingly that this is not the case. This suggests that in formulating a theory of liquids it would be well to scrutinize pretty carefully several assumptions that underlie the above considerations, namely that the temperature is proportional to the kinetic energy, that a fixed fraction of the total energy of the molecules is kinetic, and that the law of the distribution of velocities is independent of temperature.

Another quantity of thermodynamic interest which may be found in terms of the specific heats is the thermal effect of compression, that is the rise of temperature in degrees accompanying a change of pressure adiabatically of one kgm. per sq. cm. This may be computed by the thermodynamic formula $\left(\frac{\partial \tau}{\partial p}\right)_{\varphi} = \frac{\tau\left(\frac{\partial v}{\partial \tau}\right)_p}{C_p}$. The results so

calculated are shown in Figure 14 for the five standard temperature intervals. The character of the curves is the same as that shown so many times before, namely a rise to a maximum and then a fall at 0°, the abnormal behavior at the upper end of the 20° curve, and the more or less regular behavior of the three curves for the higher

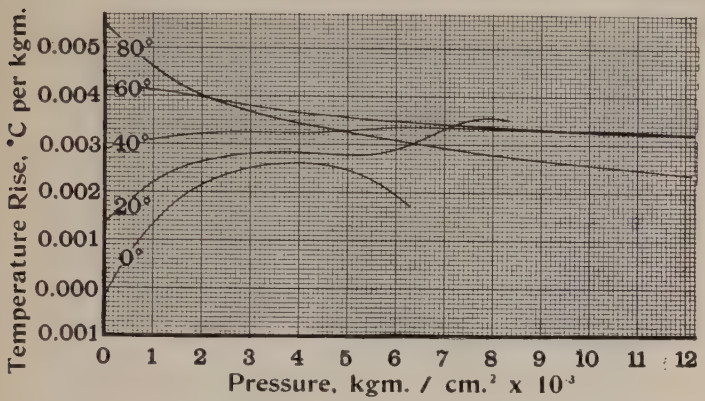

FIGURE 14. The adiabatic rise of temperature of water against pressure.

temperatures, with the crossing of the high temperature curves below the low temperature curves at the higher pressures. In the preceding paper only the approximate values for the very lowest temperature interval could be found. The calculation was based on the mean value of the dilatation between 0° and 20°. The general character of the curve was the same as that found here for 0°, namely a rise to a maximum and then a fall.

Finally it is possible to compute from the quantities in hand the difference between the isothermal and the adiabatic compressibilities. This is found from the formula $\left(\frac{\partial v}{\partial p}\right)_\varphi - \left(\frac{\partial v}{\partial p}\right)_\tau = \frac{\tau}{C_p}\left(\frac{\partial v}{\partial \tau}\right)_p^2$. The results are shown in Figure 15. The general character of the results is exactly the same as those previously given for the temperature effect of compression. Here again, the results at the lowest temperature agree with those of the previous paper which were based on a mean value for the dilatation.

Properties of Kerosene under Pressure.

In the course of the experiment other data were gathered incidentally which are of interest for themselves, and which will now be given. First of these is the compressibility and the thermal dilatation of kerosene. It was not necessary to determine this quantity in

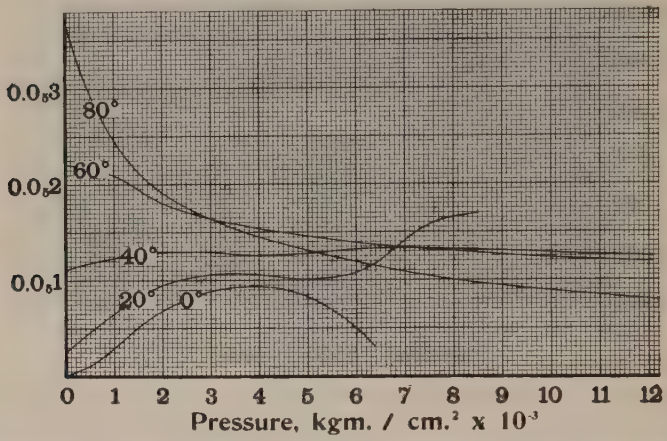

Figure 15. The difference between the adiabatic and the isothermal compressibilities of water.

order to find the corrections to be made for the distortion of the vessel, but since half the work was already done in determining the effect with the cylinder partly filled with kerosene and the other part filled with bessemer steel, it seemed worth while to make the additional run necessary to determine the pressure and temperature effects on the kerosene. Not so many determinations were made of these quantities for kerosene as were made for the water. The results are given in Table VI. The curves showing the total thermal change of volume for 20° intervals are shown in Figure 16. This figure is the analog of Figure 2 for water. The results are very different. At the lower pressures the dilatation is greater at the higher temperatures, as it is for all normal substances, but with rising pressure the effect is reversed, the dilatation becoming greater for the lower temperatures. This is the same behavior which takes place for water at higher temperatures after it has regained normality. But above 5000 kgm. the kerosene shows other abnormalities quite different in their charac-

ter from those of water. This is shown plainly in the figure as a separation and then a drawing together again of the curves. The curve for 20°–40° between 6000 and 8000 and the curve for 60°–80° beyond 9000 accomplish this separation and drawing together again

TABLE VI.

VOLUME OF KEROSENE AS A FUNCTION OF TEMPERATURE AND PRESSURE.
(The volume at 0° and atmos. pressure is taken as unity.)

Pressure, kgm./cm.²	Volume.			
	20°.	40°.	60°.	80°.
0	1.0221	1.0412	1.0611	1.0819
1000	.9643	.9763	.9885	1.0010
2000	.9274	.9376	.9468	.9553
3000	.8995	.9086	.9165	.9239
4000	.8781	.8861	.8931	.8997
5000	.8606	.8681	.8747	.8807
6000	.8456	.8529	.8592	.8647
7000	.8323	.8396	.8456	.8508
8000	.8201	.8275	.8334	.8384
9000	.8090	.8161	.8220	.8269
10000	.7989	.8057	.8115	.8164
11000	.7897	.7960	.8017	.8069
12000	.7815	.7872	.7928	7982

by rising with rising pressure, exactly as do some of the curves for water. The abnormality is doubtless due to an entirely different cause, however. In this case the effect is to be explained by the delayed freezing of the kerosene. Kerosene is not a simple pure substance, but is a mixture of several components with different melting points. Freezing under these conditions is not sharp, but is spread out over a considerable interval of temperature or pressure as the case may be. Neither is there any necessity that the freezing

should ever be perfectly complete, as indeed it is probably not. This may be shown at atmospheric pressure by plunging the kerosene into solid CO_2. The effect is to change the kerosene to a white pasty mass, like white vaseline. The pressure at which this transition occurs will rise with increasing pressure. The existence of a transi-

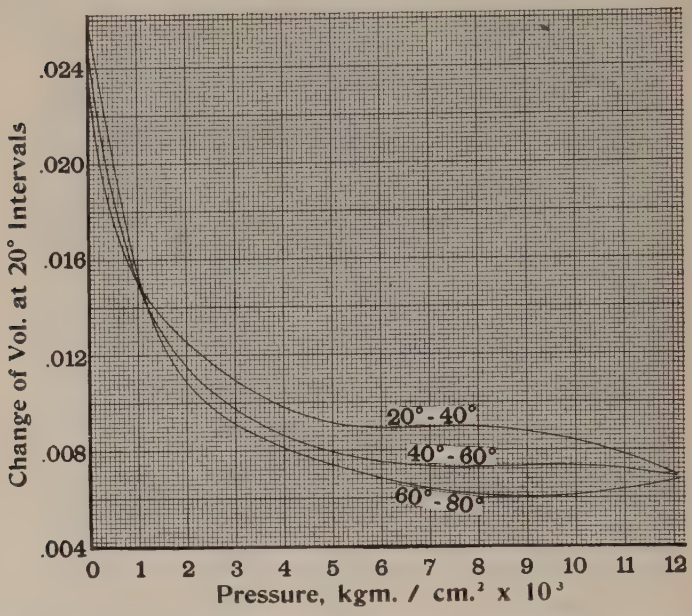

FIGURE 16. The change of volume of kerosene at constant pressure for a rise of temperature of 20°.

tion point, if there were one perfectly sharp, would be shown by an abrupt rise of the curve by an amount corresponding to the change of volume on freezing. But with the delayed freezing which takes place here due to the separation out of the separate components from a solution of varying strength, this abrupt rise becomes converted into a gradual rise extending over a fairly wide pressure range. Furthermore, the mean pressure at which this rise takes place increases with rising pressure, just as the ordinary freezing point is raised by increasing pressure. These features are all clearly shown in the diagram. At the extreme right of the diagram, at pressures over 12,000 kgm., there is evident the beginning of the reversal of the effect,

that is, the curves are going to cross again, and the thermal dilation become greater at the higher temperatures. This may possibly indicate a reversal of the reversal of the effect mentioned above for liquids, but more probably the meaning is simply that at pressure above 12,000 the substance is practically a solid, and that for solids the reversal of the effect found in liquids at high pressures does not occur.

There is one bearing which these observations have on the previous data which should perhaps be mentioned. This is in connection with the delayed freezing. Whenever freezing takes place there is usually the possibility of subcooling before separation to the solid form takes place. The amount of subcooling usually taking place depends on the nature of the liquid. In some it is very considerable, while in others it is negligible. If such subcooling took place here, it would produce irregular results, because the change of volume in the kerosene transmitting pressure to the water would not always be the same under the same pressure. The only answer to be made to this objection is that in this experiment the subcooling was not great enough to produce sensible irregularity. No discrepancies were found in the data suggesting that they were due to this effect. It was feared in the beginning of the work that the effect might be very troublesome, but such did not turn out to be the case.

Also with respect to the solidification of the kerosene, the experiments showed that the solidification could not be complete, but the kerosene, even at the highest pressures, must remain a pasty mass like vaseline in nature, always capable of transmitting pressure nearly hydrostatically. But that on the other hand the kerosene does undoubtedly become pretty stiff under pressure has been already shown in the course of some measurements on the linear compressibility of steel rods.

The second bit of data collected incidentally in the course of the work was a measurement of the expansion and the thermal dilatation of the high temperature variety of ice.

The Compressibility and Thermal Dilatation of Ice VI.

Although these data are not directly concerned with the properties of liquid water, which forms the subject matter of this paper, still it was so easy to obtain them without any modification in the arrangement of the apparatus, that it was thought worth while to measure them. In the previous paper on the properties of water and the

several varieties of ice, a very rough experimental value for the compressibility was given, as also a computation of the approximate compressibility, neglecting the thermal dilatation of the ice, for which no experimental value was found at that time. These measurements here include a direct measurement of the thermal dilatation, and two different determinations of the compressibility by two different methods. The value for the dilatation may be combined with the already determined values for the volume of the liquid and the change of volume when ice VI separates out, to give a third independent value for the compressibility.

The determinations of the dilatation will first be described. This was found in the same manner as the dilatation of the liquid, by changing the temperature at constant mean pressure, and measuring the change of pressure brought about thereby. Three determinations of this were made for the combination of ice and kerosene, and two for the combination of kerosene and bessemer. The agreement of the different determinations was within 2% of the mean. The dilatation was found between 0° and 20° at a mean pressure of 10,000 kgm. The correction introduced by the thermal dilatation of the bessemer cylinder in the control experiment is fairly large here, being about 25% of the entire effect. The value assumed for the cubic dilatation was 0.000036, which is the value for atmospheric pressure. The effect of pressure is to decrease this number slightly, which would result in a larger value for dilatation of the ice. The effect of pressure on this quantity is, however, very small, and the error so introduced is probably negligible. The mean dilatation found in this way for the 20° above 0° at 10,000 kgm. was 0.00241 cm.^{3}/ gm., or 0.000120 cm.^{3}/ gm. per degree. This is considerably less than the dilatation of the liquid in this neighborhood, for which the value 0.00040 has been found previously.

This value for the dilatation may now be combined with the other data for the liquid and the solid to give the compressibility of the solid along the equilibrium curve. For this we have the following data: vol. of 1 gm. of water at 0° and 6360 kgm., 0.8428 cm.^{3}, and at 20° and 9000 kgm. (these are the equilibrium pressures at these temperatures) 0.8160 cm.^{3}. For the change of volume when the liquid freezes to the solid we have at 0°, 0.0916, and at 20°, 0.0751. This gives for the volume of ice at the equilibrium pressures at 0° and 20° the values 0.7512 and 0.7409 respectively. The decrease of volume of the ice along the equilibrium curve is 0.0103. Part of this is an increase due to rise of temperature, which according to

the above data is 0.0024. This leaves a decrease of 0.0127 to be accounted for by the increase of pressure of 2640 kgm. which gives a mean compressibility over this range of 0.0000048, a little more than one third of the compressibility of the liquid over the same range.

The direct determination of the compressibility of the ice was made by two different methods. One of these was the same as that used roughly in the preceding paper, that is by finding the difference of the slope of the curves plotting piston displacement against pressure above and below the transition point to the solid. The values obtained in the preceding paper for this were very rough. In these determinations the cylinder was very much more carefully seasoned, and the readings were made with all the precautions which had been suggested by all the experience of this paper. Two determinations of this quantity were made at 0° and also two determinations at 20°. The two values for the difference of compressibility differed by 2.5% at 0° and by 0.7% at 20°. The value found for the difference was 0.0000087 at 0° and 0.0000067 at 20°. Combining with the values given already for the compressibility of the liquid, this gives for the compressibility of ice VI 0.0_549 at 0° and 6360 kgm., and 0.0_543 at 20° and 9000 kgm. Mean 0.0_546.

The second method for determining the compressibility was exactly the same as that for finding the same quantity for the liquid, comparing the displacements when the apparatus was filled with ice and kerosene with those when the ice was replaced by bessemer steel. This determination was made over a wider pressure range, to find if possible the variation of compressibility with pressure. No variation with pressure could be found over a range of 4500 kgm. at 0° and 3300 kgm. at 20°. The absolute values do not agree with those found by the two other methods, however, the figures being 0.0_531 at 0° and 0.0_535 at 20°. The cause of the discrepancy is not clear, but is probably connected in some way with the hysteresis of the cylinder. The hysteresis was not regular for these small pressure ranges, being at times almost negligible, and again being as large as for almost the entire pressure range from atmospheric pressure to the maximum. There seems little question but that the greater weight is to be attached to the values found by the first two methods. This third determination does show, however, that the variation of the compressibility with pressure and temperature over this range is so small as to be beyond the accuracy of these measurements. In selecting the best probable value for the compressibility the only weight that will be

assigned to this third determination is in slightly lowering the mean of the other two.

The final most probable values for Ice VI are as follows: for the compressibility 0.0_545, and for the thermal dilatation 0.000120 cm.^{3}/ gm. over the range 6360–10,000 kgm. and 0° to 20°.

The cost of much of the apparatus used in this investigation was defrayed by an appropriation from the Rumford Fund of the American Academy.

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ON THE EXISTENCE AND PROPERTIES OF THE ETHER.

By D. L. Webster.

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Presented by G. W. Pierce. Received September 12, 1912.

In the science of mechanics of ordinary matter we are accustomed to regard velocity as essentially relative but acceleration as absolute; and to say that, if a body is not acted upon in any way by other bodies, its acceleration is zero, but that, if it is acted upon by any other body, the accelerations of the two are opposite, and inversely proportional to their masses. But how can we test this law? and how can we measure the acceleration? If we measure the velocity relative to the earth, or to the sun, or to any star, at any two times separated by a very short interval, how can we be sure that the system of reference has not been accelerated during the time that has elapsed? And if it has, on what system is its acceleration measured?

This difficulty is made still more puzzling if we consider two mechanical systems, such as the solar system, exactly similar in every way, but one of which is removed to a practically infinite distance from all other matter while the other is subject to the attraction of a tremendous mass, so large and far removed that its gravitational field is practically uniform, and at absolute zero temperature so that no radiation would be received from it. These systems would be accelerated relatively to each other, but which of them would be accelerated? No observer on either of them could tell by any mechanical means.

An answer to these questions appears to be given by the electromagnetic equations, which assume the especially simple form with which we are familiar when expressed in terms of the length, mass, and time units of any one of a certain set of systems, any one of which appears to be moving relative to any other with a constant velocity, less than the velocity of light. These systems may all be assumed to be unaccelerated, and assuming the impossibility of any system's moving relative to one of these with a velocity greater than that of light, we say that all other systems are accelerated.

But acceleration means rate of change of velocity, and therefore absolute acceleration means rate of change of absolute velocity, and, if there is no such thing as absolute velocity, how can there be such a thing as rate of change of it? We must, therefore, redefine the absolute acceleration of any system to mean the acceleration relative to another system moving in such a way that the simple electromagnetic equations hold on it, and on which the velocity of the first system is zero at the instant in question.

Even now, however, there is difficulty, because in place of our set of systems with the constant relative velocities, for which the equations hold, we might equally well imagine any other exactly similar set of systems each of which has a certain given acceleration relative to the corresponding one of the first set. And, disregarding the rather arbitrary definition of absolute acceleration given above, it is evident that, if space had no properties other than those of geometry and time, any difference between the laws of nature as observed from two of these relatively accelerated systems would be impossible. But since the observed laws are simpler in one of the first set than in one accelerated relative to it, the space must have other properties than the above mentioned ones; and, because of these properties, it appears highly probable that there must be some sort of a substance, or medium, filling all space, having no acceleration relative to any of the systems for which the simple electromagnetic equations hold, not directly affecting our senses, but having properties which account for all the laws of the phenomena that are directly observable, including the exact mathematical similarity of the expressions for these laws in terms of quantities measured on any system moving with uniform velocity, less than that of light, through it. This is the medium to which we give the name of "ether."

The Ether.—To obtain any knowledge of the properties of this medium, that enable it to show the phenomena of electricity, magnetism, and gravitation, and to account for the laws of motion of matter, the principal of relativity, and the permanent existence of positive and negative electrons in spite of the possibility of collisions between them, it will be necessary to obtain the simplest possible form of the set of laws which govern these phenomena.

Since many of the quantities that we deal with are vectors, we shall find it convenient to use some simple vector analysis, with the following notation, that of Gibbs, in which all vectors will be printed in Clarendon type while scalars are in italic type. The scalar product,

$$(\mathbf{a}_x\mathbf{b}_x + \mathbf{a}_y\mathbf{b}_y + \mathbf{a}_z\mathbf{b}_z),$$

of any two vectors, $\mathbf{a}$ and $\mathbf{b}$, will be denoted by $\mathbf{a}\cdot\mathbf{b}$; while the vector product,

$$\mathbf{i}(a_y b_z - a_z b_y) + \mathbf{j}(a_z b_x - a_x b_z) + \mathbf{k}(a_x b_y - a_y b_x),$$

will be denoted by $\mathbf{a}\times\mathbf{b}$, where $\mathbf{i}$, $\mathbf{j}$ and $\mathbf{k}$ are the unit vectors in the directions of x, y, and z respectively.

The symbol ∇ will be used for the operator,

$$\left(\mathbf{i}\frac{\partial}{\partial x} + \mathbf{j}\frac{\partial}{\partial y} + \mathbf{k}\frac{\partial}{\partial z}\right),$$

so that ∇a = the gradient of scalar a, a vector; $\nabla\cdot\mathbf{a}$ = the divergence of vector $\mathbf{a}$, a scalar; and $\nabla\times\mathbf{a}$ = the curl of vector $\mathbf{a}$, another vector.

The symbol "Pot" will be used for the operation of taking the Newtonian potential of any function, so that

$$\text{Pot}\, a = \int_{\infty}\int\int \frac{a}{r}\, d\tau,$$

where r is the distance from $d\tau$ to the point at which we wish to find Pot a. We may apply the operator Pot to a vector as well as a scalar, and, in either case, Poisson's equation tells us that

$$(\nabla^2 \text{Pot}) = -4\pi,$$

or the application of the operator ∇^2 to the Pot of any function gives -4π times the original function.

It will be found convenient to indicate differentiation with respect to ct, where c is the velocity of light, by a dot over the letter that stands for the function. Thus

$$\dot{\mathbf{a}} = \frac{\partial \mathbf{a}}{\partial (ct)}.$$

For brevity let us assume also, unless otherwise stated, that the functions used in the following work all vanish at infinity and are finite and continuous throughout space.

Laws of the Ether.—To write out the laws of the ether in the form that accounts for all the above mentioned phenomena, we must distinguish between the effects due to positive and negative charges, and, therefore, it will be convenient to call the density of positive electricity at any point $\overset{+}{\rho}$, (a quantity which is always positive), and that of

negative electricity $\bar{\rho}$, (always negative). The electric forces due to all the positive and all the negative electricity we may call $\overset{+}{\mathbf{E}}$ and $\bar{\mathbf{E}}$, and the magnetic forces $\overset{+}{\mathbf{H}}$ and $\bar{\mathbf{H}}$, while the velocities of the charges may be represented in terms of $\overset{+}{\boldsymbol{\beta}}$ and $\bar{\boldsymbol{\beta}}$, their ratios to the velocity of light.

These quantities may be supposed to satisfy the following set of equations:

$$(1)\quad \nabla\cdot\overset{+}{\mathbf{E}} = \overset{+}{\rho}, \qquad (2)\quad \nabla\cdot\bar{\mathbf{E}} = \bar{\rho},$$

$$(3)\quad \nabla\times\overset{+}{\mathbf{H}} = \dot{\overset{+}{\mathbf{E}}} + \overset{+}{\rho}\overset{+}{\boldsymbol{\beta}}, \qquad (4)\quad \nabla\times\bar{\mathbf{H}} = \dot{\bar{\mathbf{E}}} + \bar{\rho}\bar{\boldsymbol{\beta}},$$

$$(5)\quad \nabla\cdot\overset{+}{\mathbf{H}} = 0, \qquad (6)\quad \nabla\cdot\bar{\mathbf{H}} = 0,$$

$$(7)\quad \nabla\times\overset{+}{\mathbf{E}} = -\dot{\overset{+}{\mathbf{H}}}, \qquad (8)\quad \nabla\times\bar{\mathbf{E}} = -\dot{\bar{\mathbf{H}}},$$

which determine the positive forces in terms of the positions and velocities of the positive charges, and the negative forces in terms of those of the negative charges. But in addition to these equations we have the following pair,

$$(9)\quad \mathbf{E} + \overset{+}{\boldsymbol{\beta}}\times\mathbf{H} + \overset{+}{\mathbf{K}} - G(\overset{+}{\mathbf{E}} + \overset{+}{\boldsymbol{\beta}}\times\overset{+}{\mathbf{H}}) = 0,$$

$$(10)\quad \mathbf{E} + \bar{\boldsymbol{\beta}}\times\mathbf{H} + \bar{\mathbf{K}} = 0,$$

which must hold at every point of every electron, positive or negative, and in which $\overset{+}{\mathbf{K}}$ and $\bar{\mathbf{K}}$ are forces per unit charge due to the internal stresses of the electron, while G is a very small number whose presence in equation (9) accounts for the phenomena of gravitation.[1]

The laws governing the vectors $\overset{+}{\mathbf{K}}$ and $\bar{\mathbf{K}}$ may be deduced from the fact that the deformation of the electron when its velocity is very great is the same as that of a perfectly flexible and compressible, charged, conducting shell, with no internal stresses, subject to a constant external hydrostatic pressure or internal hydrostatic tension.[2] Therefore, we may assume that $\overset{+}{\mathbf{K}}$ and $\bar{\mathbf{K}}$ are forces such as would result from such a tension, and that they are transmitted by

1 For further details on this point see D. L. Webster, "On an Electromagnetic Theory of Gravitation," These Proceedings, **47**, 14 (1912). The reasoning and conclusions are changed but little if we introduce a similar term in equation (10), and thereby gain in symmetry in our theory.

2 Poincaré, Comptes Rendus, **140**, 1504–8.

the material of the electron. This tension is, of course, constant throughout its volume only if all the charge of the electron is on its surface, otherwise, it increases as we go nearer the centre of the electron.

Abraham has raised the objection to this theory, that it involves an instability of the shape of the electron,[3] that would soon destroy all such bodies. But this objection is based on the interpretation of the above vectors as mechanical forces per unit charge, tending to accelerate the parts of the electrons involved, and on the idea that a part of the charge may in some way be displaced from the position in which all these forces exactly balance. Such displacements would result in a rapid disruption of the electron, a process in which equations (9) or (10) could not hold indefinitely. But if we take them as expressions of a fundamental law, which would be violated by such a process, we have a reason why this process cannot occur, nor even start to occur, and the problem of stability of shape of the electron is solved.

To determine the motion of a whole electron from these equations (9) and (10) we are aided by the fact that the resultant of the internal forces is zero, but we have to remember that the vectors $\overset{+}{\mathbf{E}}$, $\overset{-}{\mathbf{E}}$, $\overset{+}{\mathbf{H}}$, and $\overset{-}{\mathbf{H}}$, that occur in these equations, include not only the contributions from external sources, but internal as well. Therefore, the equations demand motion with constant velocity when the external forces are zero, and the resultant of the actions of different parts of the electron on each other must be zero also. But if the external forces are not zero, each part of the electron must be accelerated in such a manner that the resultant of all the forces, radiated or otherwise, from all other parts, will just balance the resultant of the external forces. Thus we have a reason for the apparent inertia of every electron, and of bodies composed of electrons, so that the laws of motion of matter may be proved to be consequences of the laws of electromagnetic forces.

Simplification of the Laws. Hamilton's Principle.

We may, however, simplify these laws still further, by remembering the fact that there is one dynamical principle that applies to all motions of matter and also to all the phenomena of slow changes of positions of electric charges and of the positions and magnitudes

3 See Lorentz, Theory of Electrons; Chap. V, 1905.

of currents, and expresses the laws of the phenomena perfectly with no other assumptions than equations (1)–(4). Therefore, it seems reasonable to suppose that this same one principle may replace equations (5)–(10), and reduce the number of necessary laws from 10 to 5.

This fundamental principle is Hamilton's Principle, which says that for any dynamical system whose kinetic and potential energies are T and W respectively,

$$\delta \int_{t_1}^{t_2} (T - W)\, dt = 0,$$

where t_1 and t_2 are any two times, and where the variation from the actual motion is any variation, consistent with the constraints of the system, that makes the configurations of the system at the times t_1 and t_2 the same as it is in the actual motion. In the case of the ether, writing $\mathbf{E}$ for $\overset{+}{\mathbf{E}} + \overset{-}{\mathbf{E}}$ and $\mathbf{H}$ for $\overset{+}{\mathbf{H}} + \overset{-}{\mathbf{H}}$, this principle takes the form,

$$(11)\quad \delta \int_{t_1}^{t_2} \int_{\infty} \{(\mathbf{H}^2 - G\overset{+}{\mathbf{H}}^2) - (\mathbf{E}^2 - G\overset{+}{\mathbf{E}}^2 + 2U)\}\, d\tau dt = 0,$$

where U is the sum of the hydrostatic tensions in the positive and negative electrons, if any, in which the element $d\tau$ lies, and which produce the forces $\overset{+}{\mathbf{K}}$ and $\overset{-}{\mathbf{K}}$, and where two configurations are to be considered the same if, and only if, the vectors $\overset{+}{\mathbf{E}}$ and $\overset{-}{\mathbf{E}}$ are the same in one as in the other.[4]

To prove that equations (5)–(6) result from equations (1)–(4) and equation (11) we may write (11) in the form,

$$(12)\quad \int_{t_1}^{t_2} \int_{\infty} \{(\mathbf{H}\cdot\delta\mathbf{H} - G\overset{+}{\mathbf{H}}\cdot\delta\overset{+}{\mathbf{H}}) - (\mathbf{E}\cdot\delta\mathbf{E} - G\overset{+}{\mathbf{E}}\cdot\delta\overset{+}{\mathbf{E}} + \delta U)\}\, d\tau dt = 0,$$

and then suppose that $\delta\mathbf{H}$, $\delta\mathbf{E}$, $\delta\overset{+}{\mathbf{E}}$, and δU are all zero throughout the interval. Now whatever vector $\overset{+}{\mathbf{H}}$ may be we may split it into a sum of two parts, $\overset{+}{\mathbf{H}}_S$ and $\overset{+}{\mathbf{H}}_L$, such that

$$\nabla\cdot\overset{+}{\mathbf{H}}_S = 0 = \nabla\times\overset{+}{\mathbf{H}}_L,$$

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[4] For another form of Hamilton's Principle, involving different assumptions see Larmor, "Aether and Matter," Chapter I.

and then write

$$\int\int\int \overset{+}{\mathbf{H}}^2 d\tau$$

as

$$\int\int\int (\overset{+}{\mathbf{H}}_S{}^2 + 2\,\overset{+}{\mathbf{H}}_S \cdot \overset{+}{\mathbf{H}}_L + \overset{+}{\mathbf{H}}_L{}^2)\, d\tau.$$

But by Green's Theorem, whatever these parts are, if both vanish at infinity,

$$\int\int\int \overset{+}{\mathbf{H}}_S \cdot \overset{+}{\mathbf{H}}_L d\tau = 0. \tag{13}$$

In this case $\overset{+}{\mathbf{H}}_S$ is completely determined by equation (3), so that, if $\delta\mathbf{E}$, $\delta\overset{+}{\mathbf{E}}$, and δU are zero, $\delta\overset{+}{\mathbf{H}}_S$ is zero, therefore

$$\begin{aligned}\int\int\int \delta\overset{+}{\mathbf{H}}{}^2 d\tau &= 2\int\int\int (\overset{+}{\mathbf{H}}_S \cdot \delta\overset{+}{\mathbf{H}}_L + \overset{+}{\mathbf{H}}_L \cdot \delta\overset{+}{\mathbf{H}}_L)\, d\tau \\ &= 2\int\int\int \overset{+}{\mathbf{H}}_L \cdot \delta\overset{+}{\mathbf{H}}_L d\tau.\end{aligned} \tag{14}$$

But this must be zero whatever $\delta\overset{+}{\mathbf{H}}_L$ is, therefore $\overset{+}{\mathbf{H}}_L$ is zero, as is $\overset{-}{\mathbf{H}}_L$ also. Therefore

$$\nabla \cdot \overset{+}{\mathbf{H}} = 0, \tag{5}$$

$$\nabla \cdot \overset{-}{\mathbf{H}} = 0. \tag{6}$$

To derive equations (7) and (8) we may introduce vectors $\overset{+}{\mathbf{I}}$, $\overset{-}{\mathbf{I}}$, $\overset{+}{\mathbf{P}}$, and $\overset{-}{\mathbf{P}}$, defined by the equations,

$$\overset{+}{\mathbf{I}} = \int_0^{ct} \overset{+}{\rho}\overset{+}{\boldsymbol{\beta}}\, d(ct), \qquad \overset{-}{\mathbf{I}} = \int_0^{ct} \overset{-}{\rho}\overset{-}{\boldsymbol{\beta}}\, d(ct), \tag{15}$$

$$\overset{+}{\mathbf{P}} = \frac{1}{4\pi}\,\mathrm{Pot}\,(\overset{+}{\mathbf{E}} + \overset{+}{\mathbf{I}}), \qquad \overset{-}{\mathbf{P}} = \frac{1}{4\pi}\,\mathrm{Pot}\,(\overset{-}{\mathbf{E}} + \overset{-}{\mathbf{I}}). \tag{16}$$

From these equations we may infer

$$\begin{aligned}\nabla^2\overset{+}{\mathbf{P}} &= -\,(\overset{+}{\mathbf{E}} + \overset{+}{\mathbf{I}}), \\ \nabla^2\overset{\cdot}{\mathbf{P}} &= -\,(\overset{\cdot}{\mathbf{E}} + \overset{\cdot}{\mathbf{I}}) = -\,(\overset{\cdot}{\mathbf{E}} + \overset{+}{\rho}\overset{+}{\boldsymbol{\beta}}).\end{aligned} \tag{17}$$

From equation (3) we know that

$$\nabla \cdot (\overset{\cdot}{\mathbf{E}} + \overset{+}{\rho}\overset{+}{\boldsymbol{\beta}}) = 0, \tag{18}$$

so that $$\frac{1}{4\pi}\nabla\cdot\mathrm{Pot}\,(\overset{+}{\mathbf{E}}+\overset{+}{\rho}\overset{+}{\boldsymbol{\beta}})=\nabla\cdot\overset{+}{\mathbf{P}}=0;$$

and since, whatever $\overset{+}{\mathbf{P}}$ is,

$$\nabla\times\nabla\times\overset{+}{\mathbf{P}}=-\nabla^2\overset{+}{\mathbf{P}}+\nabla(\nabla\cdot\overset{+}{\mathbf{P}}),$$

(19) $$\nabla\times\nabla\times\overset{+}{\mathbf{P}}=(\overset{+}{\mathbf{E}}+\overset{+}{\rho}\overset{+}{\boldsymbol{\beta}})=\nabla\times\overset{+}{\mathbf{H}},$$

which, combined with (5), gives

(20) $$\nabla\times\overset{+}{\mathbf{P}}=\overset{+}{\mathbf{H}}.$$

(21) Similarly $$\nabla\times\overset{-}{\mathbf{P}}=\overset{-}{\mathbf{H}}.$$

Equation (12) now takes the form

(22) $$\int_{t_1}^{t_2}\int_{\infty}\{(\nabla\times\dot{\mathbf{P}}\cdot\nabla\times\delta\dot{\mathbf{P}}-G\nabla\times\overset{+}{\dot{\mathbf{P}}}\cdot\nabla\times\delta\overset{+}{\dot{\mathbf{P}}})-\tfrac{1}{2}\delta(\mathbf{E}^2-G\overset{+}{\mathbf{E}}^2+2U)\}d\tau dt=0.$$

(23) But

$$\int_{t_1}^{t_2}\nabla\times\dot{\mathbf{P}}\cdot\nabla\times\delta\dot{\mathbf{P}}dt=\frac{1}{c}\nabla\times\dot{\mathbf{P}}\cdot\nabla\times\delta\mathbf{P}\Big|_{t_1}^{t_2}-\int_{t_1}^{t_2}\nabla\times\ddot{\mathbf{P}}\cdot\nabla\times\delta\mathbf{P}dt,$$

$$=\frac{1}{c}\nabla\times\dot{\mathbf{P}}\cdot\nabla\times\delta\mathbf{P}\Big|_{t_1}^{t_2}-\int_{t_1}^{t_2}[\nabla\cdot\{\ddot{\mathbf{P}}\times(\nabla\times\delta\mathbf{P})\}+\ddot{\mathbf{P}}\cdot\nabla\times\nabla\times\delta\mathbf{P}]dt.$$

(24) $\therefore$

$$\int_{t_1}^{t_2}\nabla\times\dot{\mathbf{P}}\cdot\nabla\times\delta\dot{\mathbf{P}}dt=\frac{1}{c}\Big[\int_{\infty}\nabla\times\dot{\mathbf{P}}\cdot\nabla\times\delta\mathbf{P}\,d\tau\Big]_{t_1}^{t_2}-\int_{t_1}^{t_2}\int_{\infty}\ddot{\mathbf{P}}\cdot\nabla\times\nabla\times\delta\mathbf{P}\,d\tau dt-\int_{t_1}^{t_2}\lim_{S=\infty}\int_{s}\ddot{\mathbf{P}}\times(\nabla\times\delta\mathbf{P})\cdot d\mathbf{S}dt,$$

where S is any closed surface that may recede indefinitely in all directions from any interior point, and of which $d\mathbf{S}$ is an element considered as a vector in the direction of the exterior normal. If we now let $\delta\mathbf{I}.=0$, then $\delta\mathbf{P}=0$ at t_1 and t_2, and the first term on the right side of equation (24) drops out, and so does the surface integral when there is only a finite amount of charge in the universe.

Treating $\overset{+}{\mathbf{P}}$ in the same way, we obtain, if

$$\delta\overset{+}{\mathbf{I}}=\delta\overset{-}{\mathbf{I}}=0,$$

(25)

$$\int_{t_1}^{t_2} \{(\ddot{\mathbf{P}} \cdot \nabla\times\nabla\times\delta\mathbf{P} - G\ddot{\overset{+}{\mathbf{P}}} \cdot \nabla\times\nabla\times\delta\mathbf{P}) + (\mathbf{E}\cdot\delta\mathbf{E} - G\dot{\overset{+}{\mathbf{E}}}\cdot\delta\overset{+}{\mathbf{E}} + \delta U)\}\, d\tau dt = 0,$$

or, since $\delta U = 0$ and

(26) $$\nabla\times\nabla\times\delta\mathbf{P} = -\nabla^2\delta\mathbf{P} = +\delta\mathbf{E},$$

when no motions of charges have been varied,

(27) $$\int_{t_1}^{t_2}\int_{\infty}\int\int \{(\ddot{\mathbf{P}} + \mathbf{E})\cdot\delta\mathbf{E} - G(\ddot{\overset{+}{\mathbf{P}}} + \dot{\overset{+}{\mathbf{E}}})\cdot\delta\overset{+}{\mathbf{E}}\}\, d\tau dt = 0.$$

Splitting $\mathbf{E}$ into the parts $\mathbf{E}_S$ and $\mathbf{E}_L$, treating $\overset{+}{\mathbf{E}}$ likewise, and applying Green's Theorem as in (14),

(28) $$\int_{t_1}^{t_2}\int_{\infty}\int\int \{(\ddot{\mathbf{P}} + \mathbf{E}_S)\cdot\delta\mathbf{E}_S - G(\ddot{\overset{+}{\mathbf{P}}} - \dot{\overset{+}{\mathbf{E}}}_S)\cdot\delta\dot{\overset{+}{\mathbf{E}}}_S\}\, d\tau kt = 0,$$

because $\delta\mathbf{E}_L$ and $\delta\dot{\overset{+}{\mathbf{E}}}_L$ are zero when no charge motions are varied.

(29) Therefore $$\ddot{\overset{+}{\mathbf{P}}} + \dot{\overset{+}{\mathbf{E}}}_S = 0,$$

(30) and $$\ddot{\overset{-}{\mathbf{P}}} + \dot{\overset{-}{\mathbf{E}}}_S = 0,$$

(31) or $$\overset{+}{\mathbf{E}}_S = -\frac{1}{4\pi}\,\mathrm{Pot}(\dot{\overset{+}{\mathbf{E}}} + \overset{\cdot}{\overset{+}{\rho}}\,\overset{+}{\boldsymbol{\beta}}).$$

(32) and $$\overset{-}{\mathbf{E}}_S = -\frac{1}{4\pi}\,\mathrm{Pot}(\dot{\overset{-}{\mathbf{E}}} + \overset{\cdot}{\overset{-}{\rho}}\,\overset{-}{\boldsymbol{\beta}}).$$

Applying $\nabla\times$ to (29) and (30) we have

(7) $$\nabla\times\overset{+}{\mathbf{E}} = -\dot{\overset{+}{\mathbf{H}}},$$ (8) $$\nabla\times\overset{-}{\mathbf{E}} = -\dot{\overset{-}{\mathbf{H}}}.$$

To derive equations (9) and (10) from equation (11) or (12) let us suppose that, for a short time during the interval t_1 and t_2, an *infinitesimal* positive charge de, occupying a small tube of length $d\mathbf{r}'$ and cross section $d\sigma$[5] and lying in the direction of $\overset{+}{\boldsymbol{\beta}}$ is displaced in some other direction through a distance $\delta\mathbf{r}$. To satisfy equation (1) with this variation we may superpose on the actual value of $\overset{+}{\mathbf{E}}$ a straight

[5] Any element of surface may be considered as a vector along its normal, and when its direction is chosen, the positive direction around its boundary is that of a right-handed screw rotation.

tube of the vector $\delta\overset{+}{\mathbf{E}}$ connecting the new position of de to the old, the flux of $\delta\overset{+}{\mathbf{E}}$ being against the direction of $\delta\mathbf{r}$ and of magnitude de. And to satisfy equations (3) and (5) we must also assume a certain variation $\delta\overset{+}{\mathbf{H}}$ which is uniquely defined by these equations and the variations assumed above. We may now assume no variations of the negative forces, and for the positive forces only the necessary variation of $\overset{+}{U}$ and the variations specified above.

With these assumptions (12) becomes

$$(33)\quad \int_{t_1}^{t_2}\int\int_{\infty}\int\{(\mathbf{H}-G\overset{+}{\mathbf{H}})\cdot\delta\overset{+}{\mathbf{H}}-(\mathbf{E}-G\overset{+}{\mathbf{E}})\cdot\delta\overset{+}{\mathbf{E}}-\delta\overset{+}{U}\}d\tau dt=0.$$

(34) To calculate

$$-\int\int_{\infty}\int(\mathbf{E}-G\overset{+}{\mathbf{E}})\cdot\delta\overset{+}{\mathbf{E}}d\tau,$$

we need to integrate only over the tube of $\delta\overset{+}{\mathbf{E}}$ defined above, so that, if de is of infinitesimal size, we may take for the result,

$$(35)\qquad (\mathbf{E}-G\overset{+}{\mathbf{E}})\cdot\delta\mathbf{r}de.$$

To calculate

$$(36)\qquad \int\int_{\infty}\int(\mathbf{H}-G\overset{+}{\mathbf{H}})\cdot\delta\overset{+}{\mathbf{H}}d\tau,$$

we may consider $\delta\overset{+}{\mathbf{H}}$ as the $\overset{+}{\mathbf{H}}$ produced by a current of strength $\rho\overset{+}{\boldsymbol{\beta}}\cdot d\sigma$ flowing around the edge of the parallelogram one side of which contains the old position of de and the other side the new position, while the remaining sides are the tubes of the vector $\delta\overset{+}{\mathbf{E}}$ made necessary by the motion of the parallelogram. We may now evaluate the integral, splitting the space up into elements of each of which two sides, $d\mathbf{S}$, are surfaces whose normals are in the direction of $\delta\overset{+}{\mathbf{H}}$ while the remaining dimension, $d\mathbf{s}$, is in the same direction. The integral may now be written

$$(37)\qquad \int\int_{\infty}\int(\mathbf{H}-G\overset{+}{\mathbf{H}})\cdot\delta\overset{+}{\mathbf{H}}d\mathbf{S}\cdot d\mathbf{s},$$

(38) or $$\int\int_{\infty}\int (\mathbf{H} - G\overset{+}{\mathbf{H}})\cdot d\mathbf{S}\delta\overset{+}{\mathbf{H}}\cdot d\mathbf{s}.$$

But since $$\nabla\cdot\mathbf{H} = \nabla\cdot\overset{+}{\mathbf{H}} = 0,$$

the surface integral

(39) $$\int\int (\mathbf{H} - G\overset{+}{\mathbf{H}})\cdot d\mathbf{S}$$

is the same over any cap of the parallelogram circuit as over any other; and since

(40) $$\nabla\times\delta\overset{+}{\mathbf{H}} = \delta\dot{\overset{+}{\mathbf{E}}} + \delta(\overset{+}{\rho}\overset{+}{\boldsymbol{\beta}}),$$

the line integral

(41) $$\int \delta\overset{+}{\mathbf{H}}\cdot d\mathbf{s}$$

is the same around any line of the vector $\delta\overset{+}{\mathbf{H}}$ as on any other. Therefore the integral (38) is

(42) $$\Big[\int\int_{\text{Any cap}} (\mathbf{H} - G\overset{+}{\mathbf{H}})\cdot d\mathbf{S}\Big]\Big[\int_{\text{Any line}} \delta\overset{+}{\mathbf{H}}\cdot d\mathbf{s}\Big].$$

But by Stokes' Theorem, the line integral is

(43) $$\overset{+}{\rho}\overset{+}{\boldsymbol{\beta}}\cdot d\sigma,$$

while the surface integral over the plane cap is,

(44) $$d\mathbf{r}'\times(\mathbf{H} - G\overset{+}{\mathbf{H}})\cdot\delta\mathbf{r},$$

so that (36) becomes

(45) $$\overset{+}{\rho}\overset{+}{\boldsymbol{\beta}}\cdot d\sigma d\mathbf{r}'\times(\mathbf{H} - G\overset{+}{\mathbf{H}})\cdot\delta\mathbf{r}$$

$$= \overset{+}{\rho} d\mathbf{r}'\cdot d\sigma\overset{+}{\boldsymbol{\beta}}\times(\mathbf{H} - G\overset{+}{\mathbf{H}})\cdot\delta\mathbf{r}$$

(46) $$= \overset{+}{\boldsymbol{\beta}}\times(\mathbf{H} - G\overset{+}{\mathbf{H}})\cdot\delta\mathbf{r}de.$$

Substituting $-\overset{+}{\mathbf{K}}\cdot\delta\mathbf{r}de$ for $\delta\overset{+}{U}$, (33) now becomes

(47) $$\int_{t_1}^{t_2}\{\overset{+}{\boldsymbol{\beta}}\times(\mathbf{H} - G\overset{+}{\mathbf{H}})\cdot\delta\mathbf{r}de + (\mathbf{E} - G\overset{+}{\mathbf{E}})\cdot\delta\mathbf{r}de + \overset{+}{\mathbf{K}}\cdot\delta\mathbf{r}de\}dt = C,$$

from which we may infer that

$$\overset{+}{\mathbf{E}} + \overset{+}{\boldsymbol{\beta}}\times\overset{+}{\mathbf{H}} + \overset{+}{\mathbf{K}} - G(\overset{+}{\mathbf{E}} + \overset{+}{\boldsymbol{\beta}}\times\overset{+}{\mathbf{H}}) = 0. \tag{9}$$

Obviously, we may derive equation (10) by an exactly similar process in which the terms involving G do not enter. And if we wish to use an infinitesimal charge of some other shape, we may consider it as divided up into a number of cylinders, not necessarily right cylinders, such as we used above.[6]

Meanings of the Laws.— To find out what we can about the properties of the ether, we may now examine carefully the meanings of these five laws:

$$(1)\quad \nabla\cdot\overset{+}{\mathbf{E}} = \overset{+}{\rho}, \qquad (2)\quad \nabla\cdot\overset{-}{\mathbf{E}} = \overset{-}{\rho},$$

$$(3)\quad \nabla\times\overset{+}{\mathbf{H}} = \dot{\overset{+}{\mathbf{E}}} + \overset{++}{\rho\boldsymbol{\beta}}, \qquad (4)\quad \nabla\times\overset{-}{\mathbf{H}} = \dot{\overset{-}{\mathbf{E}}} + \overset{--}{\rho\boldsymbol{\beta}},$$

$$(11)\quad \delta\int_{t_1}^{t_2}\int_{\infty}\int\{(\mathbf{H}^2 - G\overset{+}{\mathbf{H}}^2) - (\mathbf{E}^2 - G\overset{+}{\mathbf{E}}^2 + 2U)\}\,drdt = 0.$$

The first two of these laws contain no reference whatever to time, and deal with quantities whose existence is in no way dependent on motion or change with time. Therefore, we may infer that they probably express relations between the geometrical configurations of different parts of the ether, and show the dependence of these geometrical configurations upon the presence in the ether of the peculiar movable spots called charges, whose indestructibility and ability to be located definitely at different times (specified in equations (3) and (4), as well as the internal forces, suggest that they are due to the presence of some substances not present in the rest of the ether but freely movable through it. Since these substances can be located at any time if the vectors $\overset{+}{\mathbf{E}}$ and $\overset{-}{\mathbf{E}}$ are known at every point, the question arises whether any more information than the value of these vectors needs to be given to determine completely the configuration of the ether. A suggestion of the answer to this question is given by the fact that in applying Hamilton's Principle to problems of ordinary dynamics, the variations must be such as to give the actual configura-

[6] To be certain that no equations not derivable from equations (1)–(10) can be derived from (11) and (1)–(4), we need only to consider the facts that any possible variation in equation (11) can be made up of variations of the types treated above, and that the mutual energy of two independent variations of the first order is an infinitesimal of the second order.

tions exactly at the times t_1 and t_2, whereas, in equation (11) they must be such as to give the actual vectors $\overset{+}{\mathbf{E}}$ and $\overset{-}{\mathbf{E}}$. Hence, from analogy, we may say that these vectors are probably sufficient to specify the configuration of the ether completely.

And if this last statement is true, their time derivatives must be sufficient to specify completely, not only the quantities $\overset{+}{\boldsymbol{\beta}}$ and $\overset{-}{\boldsymbol{\beta}}$, but all the motions of the ether; and it seems probable that these motions at any point are specified by the values of $\dot{\overset{+}{\mathbf{E}}}$, $\dot{\overset{-}{\mathbf{E}}}$, $\overset{+}{\rho}\overset{+}{\boldsymbol{\beta}}$, and $\overset{-}{\rho}\overset{-}{\boldsymbol{\beta}}$ at that point, and not by the values of the vectors $\overset{+}{\mathbf{H}}$ and $\overset{-}{\mathbf{H}}$, which depend on the values of the other vectors at distant points. This hypothesis is further strengthened by the fact that the whole theory of the ether might be developed without any use of these vectors, replacing $\overset{+}{\mathbf{H}}$ wherever it occurs by

$$\frac{1}{4\pi}\nabla\times\mathrm{Pot}\,(\dot{\overset{+}{\mathbf{E}}}+\overset{+}{\rho}\overset{+}{\boldsymbol{\beta}}),\quad\text{and}\quad\overset{-}{\mathbf{H}}\text{ by }\frac{1}{4\pi}\nabla\times\mathrm{Pot}\,(\dot{\overset{-}{\mathbf{E}}}+\overset{-}{\rho}\overset{-}{\boldsymbol{\beta}}),$$

and therefore without any use of equations (3) and (4), except as they express the indestructibility of the charges.

Therefore we may consider equations (3) and (4) as merely equations of continuity and partial definitions of two convenient mathematical functions fully defined by equations (3) and (4) and (11) all together, and whose values at any point depend on the motions of the ether at all points, but not in any way on the motions or configurations at the point in question only. And thus, although they contain time derivatives and quantities dependent entirely on motion and existing only when there is motion, they tell us nothing about what is going to happen at some future time from what is happening now, and therefore cannot be considered as laws of motion, but only as mathematical definitions of convenient functions.

Equation (11), however, in form and substance, is essentially an equation of motion, from which no information about the geometrical configurations of the ether can be derived at any time, unless the configuration and motion at some other time, or the configurations at two other times, are specified; but without which no information about the configuration or motion at any time can be derived even if they are given at any number of other times.

Properties of the Ether. — The first question that arises about the properties of the ether is, Is its structure continuous or granular?

To answer this question definitely seems impossible, but at any rate, we can say that if it is granular and if these equations are to hold, the structure must be exceedingly minute compared to the dimensions of the electrons. A further suggestion is given by the fact that in the geometrical equations, (1) and (2), the positive and negative quantities appear very similar, but seem to be more or less independent of each other; while in the equation of motion (11), and in the phenomena of vacuum tube discharges, etc., differences between the actions of the positive and negative quantities appear, that seem to show that not only are the electrons of the different signs made up differently, but that the forces are transmitted by more or less independent, and slightly different, structures in the medium. As this condition of affairs seems to be incompatible with the idea of a continuous medium we are thereby led to the conception of a medium in which there are probably two similar, but slightly different, interlacing, granular structures, whose grains and distances between them are inconceivably small, even compared to the electrons.

The question of solid or fluid character of the ether appears easier to answer; for if it were fluid, that is, if no amount of shear at any point would change the properties at that point in such a way as to affect the subsequent motions around it, a transverse wave would be impossible. And if it were quasi-elastic, with effects analogous to viscosity, that would enable it to transmit wireless telegraph waves as well as the shortest known light waves, electrostatic forces around stationary charges should be due to some effect entirely different from that which produces those of the wireless wave, so that slow continued flow of ether might occur without hindrance. But the changes of electric force near a moving electron may be much more rapid than those of the wireless wave, and yet there appears to be no viscous retardation of its motion. Furthermore, the aberration of light and experiments such as that of H. A. Wilson [7] on the polarization of a dielectric cylinder rotating in a magnetic field seem to show that no flow of ether occurs in moving matter. These considerations and many others compel us to reject the fluid theory, and to say that the structures of the ether are solid. But by "solid" we must not mean possessed of ordinary solid elasticity, but merely that every particle is permanently connected to the particles near it by connections that cannot be deformed indefinitely, or even by a finite amount without affecting the subsequent motion.

7 H. A. Wilson. "Electric Effect of Rotating a Dielectric in a Magnetic Field," Roy. Soc. Proc., **73**, pp. 490–492. June 22, 1904.

As we must not assume ordinary elasticity, so also we must not assume ordinary inertia of the fundamental particles. For, after all, Newton's laws of motion, that we observe for ordinary matter, appear to be only approximations to the laws that result from equation (11), the more general law of motion. And furthermore, they are by no means the only ones consistent with the relative nature of time and space, nor is there any other *a priori* philosophical reason for assuming that they are true, while there is good philosophical reason for assuming that Hamilton's Principle, the mathematical expression of the perfect efficiency of the fundamental machinery of nature, is at least plausible. Therefore, whatever motions of the parts of the ether it may involve, and whether or not it is easy for us, with our Newtonian mechanical training, to form a mental picture of the dynamics of these motions, the fundamental law of the dynamics of the ether, or of any mental picture of it, must be Hamilton's Principle.

A Model of the Ether. — To get a mental picture of the actions of the ether, we must now make some arbitrary assumptions as to the nature of the two interlacing structures and the strains in them that are represented by the vectors $\overset{+}{\mathbf{E}}$ and $\overset{-}{\mathbf{E}}$. For simplicity we may think of them as nets with cubical meshes with each knot of either net in the centre of a mesh of the other, wherever the electric vectors are zero. The vector $\overset{+}{\mathbf{E}}$ may be a very minute displacement of one of these nets from this position, and the vector $\overset{-}{\mathbf{E}}$ the negative of a similar displacement of the other. If we now suppose the strings of these nets to be hollow and rigid, and the knots to be hollow boxes, so constructed that the displacements of the nets will be those of an incompressible substance, we may suppose an electric charge to be a region in which the pipes and boxes of one of the nets are filled with a liquid of high surface tension, that will expand the boxes into which it flows, and cause a divergence of the displacement of the net. An electron will then be a region of this sort, in the shape of a hollow sphere when at rest, of which every dimension, including the thickness, is very large compared with the meshes of the net. The pipes and boxes of that net that lie inside this region may be filled with a fluid whose only properties are adhesion with everything it touches and a constant hydrostatic tension, independent of its volume. For the connections between the nets we may assume anything we please.

Equations (1) and (2) are satisfied by this model, which also gives an interesting interpretation for (3) and (4). For in free ether the

vector $\overset{+}{\mathbf{H}}$ becomes a hydrokinetic flow-function for the motion of the positive net; and where there is any positive charge it is a flow-function for the motion of the net plus that of the charge. Similarly the vector $\overset{-}{\mathbf{H}}$ is the negative of a flow-function of the motion of the negative net and charges. And in each case, equations (5) and (6) tell us that it is the solenoidal flow-function that is required.

The equation of motion is, as we expected, one which we have some difficulty in applying. But if we split it up into equations (5) to (10), and then combine them properly, we may use in electrical problems only the vectors **E** and **H**, representing the *relative* displacement of the positive net from the negative, and the flow-function of the *relative* motion. And in gravitational problems the vectors **E** and **H** disappear entirely.

Collisions of Electrons. — An interesting application of this model is to the problem of collisions of electrons, of the same or opposite signs, as in the case of a cathode particle striking an electron in the metal it hits. If they are of the same kind they will evidently become flattened as they come together. But as soon as they are within about their own length of each other, the side of either of them nearest the other will be effected not only by the displacement due to the presence of the other, but also by the displacements radiated from the other on account of its acceleration. To make the vectors balance, as required by equations (9) and (10), its acceleration must therefore be so much greater than that required by the inverse square law that they can never collide.

In the case of two electrons of different kinds, both are lengthened, and they come together faster than the inverse square law would demand. But since they may go right through each other perfectly freely, there need not be any of the destructive effects that one might expect from other theories.

Retarded Potentials.[8] — In calculating the values of the retarded potentials due to moving electrons it is found necessary to treat each electron as if its charge were not the same as when at rest, but changed in the ratio $(1 - \beta_r)^{-1}$, where β_r is the component of $\boldsymbol{\beta}$ in the direction towards the point at which we wish to know the potential. This has been interpreted by some writers [9] as indicating that all electromagnetic actions are due to some sort of pulsation of the electrons, and are

[8] For information about retarded potentials, see Lorentz, "Theory of Electrons," Chap. 1.

[9] L. de la Rive, Phil. Mag., **13**, p. 279.

stronger if the pulsations are more rapid, so that the Doppler effect is introduced if the charge is moving. But with the model it is obvious that any such interpretation is unnecessary; for the important quantity is not the actual charge of the electron, but the volume of the ether in which there was a spreading of the net at such a time as to affect the point in question at the time in question.

Summary.

Because of the apparently absolute nature of acceleration, as well as for other reasons, we find it necessary to assume the existence of the ether, and therefore desirable to learn as much as possible of its properties. To do this, we first reduce the laws of all its phenomena, including gravitation and the relativity-principle, to five equations, and then examine their meanings; and find that two of them are probably laws of the geometrical configurations of the different parts of the ether; two more, equations partially defining two convenient vectors, and stating the indestructibility of electricity; while the fifth, Hamilton's Principle, is a law of motion, expressing the perfectly efficient cooperation of the different parts of the fundamental mechanism of the universe.

From these laws we may draw certain conclusions about the structure and properties of the ether, which are not, however, enough to enable us to determine exactly what it is. But by a few simple assumptions, we obtain an imaginable model of its actions. And since the model is based directly on the electromagnetic laws, it may be applied, without fear of error, to any electromagnetic problem, to enable us to obtain a qualitative result without mathematical analysis.

THE THEORY OF THE SCATTERING OF RÖNTGEN RADIATION

By D. L. Webster *

IN a recent paper by Mr. J. A. Crowther, † are described some experiments on the scattering of Röntgen rays by disks of aluminium or paraffin paper, made to test the formula that gives the intensity of the rays scattered to an angle θ as proportional to $(1+\cos^2\theta)$. This formula may readily be obtained from the expressions for the radiated electric and magnetic vectors given by Professor Sir J. J. Thomson in his book, ' The Conduction of Electricity through Gases,' with the assumption that each electron in the radiator scatters the same amount of energy that it would scatter if it were alone.

The observed radiation is found to fit the formula well at angles greater than about 60°, but to be much in excess of the calculated value at small angles. The properties of this excess radiation are summarized in a second paper by Mr. Crowther, ‡ as follows: —

" (1) For a given radiator and for primary rays of given hardness the excess radiation in any direction is directly proportional to the thickness of the radiator.

" (2) The total excess radiation round the radiator decreases as the primary beam becomes harder, and increases with the atomic weight of the radiator.

" (3) Within the limits of experimental error the hardness of the excess radiation is the same as that of the primary from which it is produced.

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* Communicated by Dr. Theodore Lyman.

† Proc. Roy. Soc. A. lxxxvi. pp. 472–494.

‡ Proc. Camb. Phil. Soc. xvi. 6, pp. 534–539.

" (4) If $E_\theta \delta\theta$ is the intensity of the excess radiation between the angles θ and $\theta + \delta\theta$ with the primary beam.

$$E_\theta \delta\theta = \frac{2}{b} E e^{-\theta^2/b} \theta \, \delta\theta,$$

where E is the whole intensity of the excess radiation round the radiator, and b is a constant depending only on the quality of the primary beam and the substance of the radiator.

" (5) The value of b decreases as the primary beam becomes harder, and increases with the atomic weight of the radiator. It is independent of the thickness of the radiator."

In Mr. Crowther's first paper these effects were explained by the hypothesis that each molecule refracted part of the rays falling on it through a certain small angle, and the distribution of the excess radiation was shown to agree with the distribution calculated on this hypothesis by Professor Thomson. But in the second paper another explanation, on the basis of radiation from the stoppage of secondary cathode particles, was put forward.

The purpose of the present paper is to revise the original formula without the hypothesis that each electron scatters energy exactly as if it were alone, and to show how the re-enforcement of the radiation from one electron by that from another may produce the " excess radiation " that Mr. Crowther has observed.

For this purpose, we may first consider a single, polarized, primary pulse, specified by the formula

$$E_z = E_x = 0, \quad E_y = E_0 f\left(\frac{t-x}{T}\right); \quad . \quad . \quad . \quad (1)$$

where t is the time, considered equal to the distance light has gone since the time $t = 0$. Let $f(s)$ be zero except in the interval $-\frac{1}{2} < s < +\frac{1}{2}$, over which the average value of its square is 1, so that E_0 is the square root of the mean square of E_y. Let there be n electrons per unit volume in the radiator, each with a charge ϵ and mass m *; and let the origin of coördinates be the position of one of the electrons at the time $t = 0$.

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* It must be noticed here that with the time unit used in this paper, to make force equal to mass times acceleration, the mass of any body must be c^2 times the mass in units in which the velocity of light is c.

At the point $r, \theta, \frac{\pi}{2}$, in the x, z plane, where r is very large compared with the distance of any electron in the radiator from the origin, and $z>0$, the electric vector radiated from an electron at x, y, z, is in the $-y$ direction, of intensity,

$$\frac{\epsilon^2 E_0}{4\pi m r'} f\left(\frac{t-r'-x}{T}\right), \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where r' is the distance from the electron to the point x, y, z.

For the electron at the origin, letting $E_1 = \epsilon^2 E_0/4\pi m r$, this reduces to

$$E_1 f\left(\frac{t-r}{T}\right). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2')$$

Neglecting small quantities of the second order, (2) becomes

$$E_1 f\left(\frac{t-r-x(1-\cos\theta)+z\sin\theta}{T}\right). \quad . \quad . \quad . \quad (3)$$

If now the electron at the origin is to be re-enforced by the one at x, y, z, the times of arrival at $r, \theta, \frac{\pi}{2}$ of their scattered radiations must differ by less than T, so that the point x, y, z must at least lie between the planes,

$$\left.\begin{aligned} x(1-\cos\theta)-z\sin\theta &= -\tfrac{1}{2}T, \\ \text{and} \qquad x(1-\cos\theta)-z\sin\theta &= +\tfrac{1}{2}T, \end{aligned}\right\}, \quad . \quad . \quad . \quad (4)$$

the distance between these planes being $T/2 \sin\frac{\theta}{2}$, and their direction being parallel to the y axis and to the bisector of the angle between the x axis and the radius vector r.

This, however, is not the only limitation on the space available for re-enforcing electrons, for there is also the limitation due to the second order terms, neglected in (3). But since the limits thereby imposed may be widened indefinitely by making r large enough, we shall disregard this limitation.

But another limitation, that cannot be disregarded, is imposed by the irregularities of the primary pulse, due to the disturbing effects of electrons near the $-x$ direction from the region considered. To determine the shape of the space to which we are limited by this effect, we have no data except the fact that each electron disturbs the primary pulse only throughout a very sharp cone with its

apex at the electron and its axis in the x direction from it. For a rough approximation we may assume the region to be a sphere with a number of these practically cylindrical pieces cut out of it; and for purposes of computation the result may be assumed to be a spheroid, flattened in the x direction, with its centre at the origin.

If we knew the equation of this spheroid, we might now calculate the volume, V, that lies at the same time within the spheroid and between the planes of equations (4). But any accuracy in such a calculation would be worthless when combined with the approximations already made, and a qualitative analysis of the behaviour of V as a function of θ is more useful.

As the thickness, T, of the primary pulse may be supposed fairly small compared with any radius of the spheroid, at least if the material is not too dense and n not too large, V may be considered as the product of the distance $\mathrm{T}/2 \sin \frac{\theta}{2}$, between the planes by the mean area of the sections of the spheroid parallel to the planes and included between them. Since the inclination of the planes to the x axis is $\frac{\theta}{2}$, this mean area will be a maximum when θ is 180°, and will decrease, slowly at first, then more rapidly, as θ decreases. But since the thickness of the segment increases, slowly at first, and then more rapidly, V may change very slowly until θ is fairly small. At this stage of the process the rate of change of the mean area will diminish, while the thickness continues to increase faster than before. The volume will now begin to increase and continue to do so until the whole spheroid is included between the planes, and no further increase is possible.

From the experimental fact that the scattered radiations are about as hard as the primary, we may be sure that, when θ is large, V must be small enough to contain rarely more than one electron, or cluster of electrons, if they are in compact clusters; for if there were many electrons, or clusters, radiating only slightly out of phase, the resultant radiation would appear as a pulse thicker than the primary. If there are such clusters, the charge, ϵ, and mass, m, must be the charge and mass of the whole cluster.

In either case, if one such charge is known to be in the volume V, the probability of there being no other there is e^{-nV}; so that of all the secondary pulses scattered per unit volume of the radiator, ne^{n-V} may be supposed to have electric vectors specified by expression (2), and to scatter energy per unit area at the distance r equal to

$$E_1^2 ne^{-nV} \int_{-\infty}^{+\infty} \left[f\left(\frac{t-r}{T}\right) \right]^2 dt = E_1^2 T ne^{n-V} \quad . \quad . \quad . \quad . \quad (5)$$

Of the $n(1-e^{-nV})$ charges per unit volume not radiating alone, to which expression (5) cannot be applied, a fraction e^{-nV} may be supposed to radiate in pairs only, each pair giving an electric vector in the $-y$ direction, of intensity,

$$E_1 \left[f\left(\frac{t-r}{T}\right) + f\left(\frac{t-r'-x}{T}\right) \right], \quad . \quad . \quad . \quad . \quad (6)$$

where the origin is on one of the electrons of the pair. Squaring and integrating with respect to t, we find for the energy scattered per unit area from each pair

$$2E_1^2 T(1+F), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where F is the mean product of the functions f for pairs of which one electron is at the origin, while the other may be in any part of the volume V with no preference for any part over any other. Evidently F is constant for large values of θ, but variable, increasing as θ decreases, at smaller angles, but always remaining less than (1).

The case of three electrons in the volume V presents no additional difficulties, except the introduction of the mean product F′ of the functions f for pairs of which both members are scattered indiscriminately over the volume.

We may now discard the assumption of a single, polarized, primary pulse, and assume that there are N primary pulses per unit time, and that the mean square of the z component of the primary electric vector is the same as that of the y component, where the mean is over a long time, rather than over a single pulse. This change in our assumptions must, of course, result in the introduction of a factor $N(1+\cos^2\theta)$ into the expression for the scattered radiation, to obtain the total energy scattered per unit

time, per unit area of the receiving screen at a distance r, and per unit volume of the radiator. The resulting quantity, which takes account of all re-enforcements of radiations, is

$$E_1^2TN\,(1+\cos^2\theta)ne^{-nV}[1+(1+F)\,(1-e^{-nV}) + (1+F+F')\,(1-e^{-nV})^2+(1+F+2F')\,(1-e^{-nV})^3+\ .\ .\ .\ .]. \quad (8)$$

To obtain what Mr. Crowther terms the "excess radiation," we may subtract from expression (8) the value, $E_1^2TnN\,(1+\cos^2\theta)$, of the same quantity calculated without reference to re-enforcements of the radiations. And since, for large values of θ, n V is very small, and the excess radiation extremely small, the total excess radiation between the angles θ and $\theta + d\theta$ may be obtained by multiplying this result by $2\pi r^2\theta\,d\theta$, so that the final value of the excess radiation becomes

$$\left.\begin{aligned} &2\pi r^2E_1^2TNn(1+\cos^2\theta)e^{-nV}[F(1-e^{-nV})+(F+F')\,(1-e^{-nV})^2 \\ &\qquad +(F+2F')\,(1-e^{-nV})^3+\ .\ .\ .\ .]\theta\,d\theta \\ &= \frac{\epsilon^4E_0^2TNn}{8\pi m^2}\,(1+\cos^2\theta)\,(1-e^{-nV})\,[F+(e^{nV}-1)\,F']\theta\,d\theta,* \end{aligned}\right\} \quad (9)$$

where by excess radiation we must mean the energy scattered per unit volume of the radiator per unit time in the whole solid angle between θ and $\theta + d\theta$, in excess of the value for the same quantity calculated from the simpler formula.

On account of our lack of knowledge of the values of many of the quantities occurring in this expression, it is impossible to compute the amount of this radiation. To test the theory, let us therefore compare the changes of this quantity with those found experimentally by Mr. Crowther for the real excess radiation.

The first of his statements, of proportionality of the excess radiation to the thickness of the radiator, is obviously true of

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* Note that

$$e^{+nV} = \frac{1}{e^{-nV}} = \frac{1}{1-(1-e^{-nV})} = 1+(1-e^{-nV}) + (1-e^{-nV})^2+(1-e^{-nV})^3+\ \ldots,$$

and that

$$e^{+2nV} = \frac{1}{(e^{-nV})^3} = \frac{1}{[1-(1-e^{-nV})]^2} = \frac{d}{d(1-e^{-nV})}\left(\frac{1}{1-(1-e^{-nV})}\right) = 1+2\,(1-e^{-nV})+3\,(1-e^{-nV})^2+4\,(1-e^{-nV})^3+\ \ldots$$

the calculated value, which is a certain quantity per unit volume of the radiator.

By making the primary beam harder, keeping E_0^2TN constant, the volume V is diminished at any given angle, so that the excess radiation, which increases with V, is thereby diminished. On the other hand, an increase of atomic weight, if it means an increase of n, must increase the excess radiation. The second condition is therefore satisfied.

The agreement of the formula with Mr. Crowther's third statement is apparently not so good, as it seems as if, when the pulses from two neighboring electrons arrived at the observing point at times differing by some fraction of T, the resulting radiation might not be quite so hard as the primary. But it may be that this effect would be too small to be detected experimentally.

The agreement of the expression (9) with Mr. Crowther's formula for the scattered radiation depends of course on the way in which V, F, and F′ vary with θ; but on careful examination it may be seen that some variations of the sort specified above will suffice.

The fifth statement, about the changes of b, is equivalent to a statement that as the primary beam becomes harder, the excess radiation will be confined more and more to the smaller angles. This is obviously equally true of the calculated value, as an increase of hardness, and consequent decrease of T, makes V begin to decrease sooner with increase of θ, and confines the re-enforced radiations to smaller angles.

While it seems probable from these considerations that no further assumptions than the existence of electrons and the truth of the electromagnetic equations as applied to them are necessary to explain most of the effects observed by Mr. Crowther, it is by no means certain that the secondary cathode particles of which he speaks in his second paper do not have an important effect upon the phenomena. But as his hypothesis is based partly on the assumption that a cathode particle radiates only when being stopped, and then only in the direction of its motion just before stoppage, the accuracy of his conclusions must depend partly on the accuracy of this assumption. On this the equations of the electromagnetic field lead to some interesting suggestions.

For if an electron already in rapid motion is accelerated in any direction, and the retarded potentials due to it are computed for any point in the radiated pulse, they will both contain the factor $(1-\beta_r)^{-1}$, where β_r is the component of the velocity of the electron in the direction of the point considered, the time units being the same as above. Therefore, as a brief calculation would show, the radiated vectors would differ from the values for the case of an electron momentarily at rest by the same factor, and the radiated energy per unit volume of the pulse by the square of this factor. But the thickness of the pulse varies directly as $(1-\beta_r)$. Hence the radiation per unit area of the pulse will be stronger in the ratio

$$\left(\frac{1+\beta_r}{1-\beta_r}\right), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

in this direction than in the opposite. To the extent indicated by this ratio, and only to this extent, may we therefore say that the Röntgen pulse follows the direction of the cathode ray from which it is produced.

The results of the experiments by Mr. Kaye,* quoted by Mr. Crowther as a confirmation of his hypothesis, are easily explained by expression (10). For in these experiments it was found that if cathode rays were allowed to strike a very thin metallic anticathode, the intensity of the Röntgen radiation in a direction near that of the cathode beam was much greater than in the opposite direction, the ratio in the case of an aluminium anticathode being sometimes as great as 3·2, indicating a mean velocity of the radiating electrons of nearly ·5. As Mr. Kaye does not say what the velocity of his rays was, a direct comparison with the calculated velocity is impossible; but indeed it would be a very poor check on the accuracy of the assumptions, for the opposing influences of the retardations and deflexions of the cathode particle, that diminish the effect, and the increase of its velocity on close approach to a positive electron (the only kind that can cause appreciable radiation), may produce great changes in the velocity of an electron before it radiates. But the order of magnitude of the effect, as well as an observed difference in hard-

* G. W. C. Kaye, Proc. Camb. Phil. Soc. xv. p. 269 (1909).

ness of the rays, to be accounted for by the well-known Doppler effect, does much to confirm this hypothesis.

From these results it appears that the secondary cathode particles, while they must produce some radiation, possibly a part of Barkla's homogeneous secondary radiation, cannot produce any distributed like the secondary radiation on which Mr. Crowther's experiments were performed. And since the results of his experiments, as well as those of Mr. Kaye, are well accounted for by the theory of Röntgen rays as electromagnetic pulses, and are necessary consequences of this theory, they are also important confirmations of its fundamental assumptions.

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CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL LABORATORY OF HARVARD UNIVERSITY.

THERMODYNAMIC PROPERTIES OF TWELVE LIQUIDS BETWEEN 20° AND 80° AND UP TO 12000 KGM. PER SQ. CM.

By. P. W. Bridgman.

With seven Folders.

Investigations on Light and Heat made and published with Aid from the Rumford Fund.

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By P. W. Bridgman.

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I. Introduction.

The experimental material of this paper consists of direct measurements of the volume of twelve liquids at different temperatures and pressures. The pressure range is from atmospheric pressure to 12000 kgm. per sq. cm., and the temperature range from 20° to 80°. The measurements were made at enough points to determine the volume at any pressure and temperature. These data are presented in the first part of the paper. The second part of the paper contains a discussion of a number of quantities of thermodynamic significance which have been computed from the data of the first part. The discussion is concerned only with the more important thermodynamic properties, namely the isothermal compressibility, thermal expansion, work of compression, heat of compression, change of internal energy, and the specific heats at constant pressure and constant volume.

Apparently the only other work of similar character at even comparatively high pressures is that of Amagat,[1] published in 1893. Amagat measured the volume of twelve liquids up to 3000 kgm. and between 0° and 40° or 50°. Beside the volume he tabulated the compressibility, dilatation, and pressure coefficient for some of the liquids, but the tabulation was by no means systematic or complete.

It is hoped that the material in this paper will afford the means for a renewed attack on the problem of the nature of the mechanism of a liquid. Theoretical speculation has been concerned hitherto chiefly with phenomena of liquids at low pressures, such as the latent heat of evaporization or the surface tension. At high pressures there are effects of another order, just as significantly descriptive of the internal mechanism, but as yet hardly touched by speculation. The data of this paper cover four times any previous pressure range, and should be sufficient to show the general nature of high pressure effects. Furthermore, the systematic presentation of different thermodynamic properties should afford different points of view for the attack.

The actual state of affairs at high pressures was found to be exceedingly complicated, contrary to what we might expect. We might suppose that the molecules would become so closely packed at high pressure as to allow less variety in their response to external changes, so that a liquid would approximate to a solid, in which compressibility and expansion change only slightly with pressure and temperature. A hypothesis of this character, backed up it is true by some experi-

[1] Amagat, Ann. Chim. et Phys., **29**, 68–208 (1893).

mental evidence, has been made the basis of a recent empirical theory of liquids by Tammann,[2] who assumes that at high pressures variations in thermal expansion due to changes of temperature ought to become vanishingly small. Such, however, is by no means the case, but, on the contrary, at high pressures the thermal expansion varies with temperature in a more complicated way than at atmospheric pressure.

The irregularity of the effects at high pressures makes it evident that a complete theory of liquids must be very complicated. The first step, therefore, toward a theory would be to explain only the general features. With this in mind, the average of the various thermodynamic properties over the entire temperature range has been computed for each liquid. To facilitate comparison, the average of any one property, compressibility for example, is shown on the same diagram for all twelve liquids. One would expect to turn at first to these collected diagrams in seeking light on a theory of liquids.

In this paper no attempt has been made at the very considerable task of developing a quantitative theory to represent the data. The results suggest very strongly in some cases, however, that conceptions of the mechanism of a liquid which may be adequate at low pressures can no longer be adequate at high pressures. For instance, we shall probably have to modify our ideas of the mechanism accounting for pressure and temperature. Some discussion is given of modifications that may be necessary, and in several cases it is shown that the proposed modifications are competent to explain, at least qualitatively, the complicated effects found at high pressures.

A preceding paper on water[3] is very similar to the present one in the scope of its measurements and computations. The hope was expressed in the introduction to that paper that the projected study of twelve liquids (that is, this paper) would show what we might expect of a normal liquid, and that the results for water might then be compared with these results, and yield information about the abnormalities of water. This hope now appears to have been unfounded because no liquid is really normal at high pressures; all show individual peculiarities. It is true, nevertheless, that at high pressures these twelve liquids do become more nearly alike in a general way, and that water becomes increasingly like them. In many cases it will be found instructive, therefore, to compare the properties of water at high pressures with those of the liquids of this paper.

2 Tammann, Ann. Phys., **37**, 975–1013 (1912).
3 Bridgman, These Proceedings, **48**, 307–362 (1912).

The initial abnormalities of water have such a far-reaching effect, however, up to 6000 kgm., that it seemed desirable not to include water directly in the same diagrams with the other liquids.

The apparatus and the experimental method are in large measure the same as were used in the preceding work on water, and will not be described again in any detail. The methods of computation, however, are somewhat different, and are discussed at some length. It is impossible to give the original data because of lack of space. However, a few sample curves of the original data are given, and the average error of the compressibility and the expansion measurements is stated for each liquid.

The liquids used are with two exceptions the same as those used by Amagat. This choice of liquids has two advantages. In the first place, the present method does not give accurate results at the very lowest pressures, so that it is desirable to supplement the measurements with others at low pressures. For this purpose the values of Amagat for the change of volume between atmospheric pressure and 500 kgm. have been used. And in the second place, it was not desired to complicate this study, which is concerned with the liquid only, by the possibility of freezing under pressure. The freezing points of all the liquids used here are very low. It was hoped, therefore, that none of them would freeze under pressure at the temperatures of this investigation. The anticipation of no freezing was justified except in the case of acetone, which, however, froze at such high pressures that it was not necessary to discard it.

Comment should perhaps be made on the very extensive use of diagrams instead of tables. A table is capable of greater accuracy than a diagram, but a diagram has the advantage of presenting a large collection of results in a form immediately grasped. By the use of diagrams with fine rulings, the attempt has been made to combine the general grasp afforded by a diagram with the accuracy of a table. In most cases the numerical values may be read directly from the diagrams within the limits of experimental accuracy. The only exception is for the fundamental data, volume against pressure and temperature, for which tables have been given to four significant figures. The diagrams accompanying these tables are quite secondary in importance, giving merely a general survey of the trend of the results.

A brief indication of the plan of presentation may be helpful to the reader. The apparatus and the experimental method are first briefly described, indicating the points of departure from the previous

work on water (pages 7 to 18). Then the methods of computation are taken up in detail, describing in succession the method used for each one of the thermodynamic properties (pages 18 to 37). A somewhat detailed analysis of the data for each liquid is next given, including any special features of the experiment for that liquid, the experimental error, and the source and probable accuracy of data by other observers which have been used in the computations (pages 37 to 74). Here are included the fundamental data for each liquid, that is, the tables and diagrams of volume against pressure and temperature. The various thermodynamic properties are then discussed, with comments on the peculiarities of the individual liquids, and on the general features common to them all (pages 74 to 104). The diagrams for this general discussion are given on folders at the end of the paper, all the diagrams for any one property being collected on one sheet. It is hoped that this arrangement will produce less confusion in the text, and at the same time, permit a more ready general survey of the facts. Finally, there is given on pages 104 to 113, a discussion of the bearing of the results on previous theories, and of the possible effects on our ideas of what the actual mechanism of a liquid may be.

II. Experimental Method.

The method is essentially similar to that used in the preceding work on water. As in the earlier work, so here, the liquid under investigation is placed in a cylinder closed by a piston which moves absolutely without leak. The pressure on the liquid may be varied by changing the position of the piston, and the temperature may be varied by altering the temperature of the surrounding bath. The volume is found directly by measuring the position of the piston in the cylinder. The fundamental data to be obtained with the apparatus are the values of the volume as a function of pressure and temperature at a sufficient number of points to allow the calculation of the volume at any temperature and pressure within the range.

In actual use the simple procedure suggested above is complicated by the necessity of introducing the instrument for measuring the pressure into the same cylinder with the liquid under investigation. The pressure in these experiments was measured with a coil of manganin wire, the changes in the resistance of which give the pressure by a previous calibration.[4] Although this manganin gauge is compact

[4] Bridgman, These Proceedings, **47**, 319–438 (1911).

and simple, its use introduces complications, because it must come in contact only with a liquid that is an insulator. The water of the preceding paper and nearly all the twelve liquids of this are not insulators. Some auxiliary liquid must be used therefore, to transmit pressure to the manganin coil. Kerosene has shown itself perfectly adapted to the purpose, and has been used in all this work. In the former work on water, the kerosene and water could be allowed to come directly in contact with each other, but in this investigation, nearly all the liquids are more or less miscible with kerosene, so that means had to be provided to prevent the liquid under investigation from coming into contact with the kerosene. This necessitated slight changes in the design of the apparatus, and the use of still a third liquid, mercury, to keep the liquid and the kerosene from direct contact. The modified receptacle for holding the liquid is shown in Figure 1. The liquid is enclosed in a steel bulb A, the stem of which dips into the cup B containing mercury. The cup B is bored out at the lower end so as to protect the manganin pressure gauge, which is shown at C. The bulb, cup, and gauge together occupy the lower part of the pressure cylinder. In order to obtain as large a quantity as possible of the liquid to experiment on the diameter of the bulb etc. was made larger than that of the moving piston ($1\frac{1}{8}$ inch against $\frac{1}{2}$ inch). To allow this the cylinder had to be bored out at the lower end to the larger diameter. In other respects the cylinder is similar to that used for water, in fact it is the same cylinder, the only change being the enlargement of the lower part to meet the new requirements.

FIGURE. 1. The compressibility bulb with attachments. *A* is the bulb containing the liquid under investigation, *B* the mercury cup, and *C* the insulating plug and the manganin coil with which pressure is measured.

The final form of receptacle shown in Figure 1 was arrived at only after a considerable number of failures. Early attempts to use glass cylinders, which from the point of view of purity would be more desirable, had to be abandoned because of the invariable fracture of the glass. This is doubtless because kerosene under pressure becomes

so viscous as not to transmit small changes of pressure hydrostatically immediately after changes in the position of the piston. The enormously increased viscosity both of the kerosene and of the liquid under investigation within the bulb afforded the only satisfactory explanation of many of the capricious misfortunes of the preliminary work. For instance, in the early work the bulb was closed at the upper end by a cap put on with soft solder. Several times after the application of pressure this soft solder was found eaten away by the mercury. The only apparent way in which this could happen would be by the liquid (ethyl alcohol in the preliminary investigations) becoming so viscous as to crack as the volume decreases with rising pressure, thus allowing the mercury to rise through the cracks from below. Another very troublesome effect in the preliminary work was the frequent short circuiting of the manganin coil by small drops of mercury. These were probably forced out of the cup by the viscous motion of the kerosene during changing pressure. The difficulty was avoided by making the lower part of the mercury cup in the form of a protecting cap for the manganin coil, and by enlarging the channels of communication between the cup and the bulb from the kerosene to the mercury. It was found also that it was necessary to give the bulb fairly thick walls. Otherwise, when pressure is relieved, the bulb expands under the viscous motion of the fluid inside and tightly fills the cylinder. Furthermore, the bulb must not fit the cylinder too closely, for otherwise the pressure is not transmitted rapidly enough to the interior of the bulb, which may thereby become collapsed at the upper end. Still again, the upper end of the bulb must be provided with radial grooves to give access from the lower to the upper part of the cylinder, or else when pressure is released, the entire bulb rises with the viscous kerosene against the ledge on the cylinder, acting effectively as a valve which permits only comparatively slow release of pressure, with the result that eventually, when pressure is released, the top is blown off the bulb and forced into the smaller bore of the cylinder above.

It must be a matter of experiment to find the dimensions for any particular piece of apparatus which will avoid all these difficulties. Complete success was attained, however; the last twenty out of a total of twenty-four runs being completed without accident of any kind.

Although the method outlined above is exceedingly simple, yet there are evidently a number of corrections for the distortion of the steel

containing vessel and for the auxiliary liquid. These corrections have been discussed in great detail in the preceding paper on water. The corrections to be used in this paper are exactly similar to the former ones, with the exception of the correction for the effect of the mercury. It will be recalled that two sets of measurements are necessary to obtain all the data needed in making the corrections; the first is with the steel bulb filled with the liquid under investigation, and the second with the liquid and bulb replaced by a cylinder of Bessemer steel. The quantities of kerosene are approximately the same in the two sets of measurements. If the quantity of mercury used in the two sets were exactly the same, it would not be necessary to apply any correction for it, but since it was not easy to use exactly the same quantity, a correction for the difference had to be applied. This correction was exceedingly small, being merely the change with pressure and temperature of the small difference, and could be obtained with sufficient accuracy for this purpose from measurements already made on mercury up to 12000 kgm. at 0° and 20°.[4] The variation of compressibility and dilatation with temperature is so small at high pressures that it is perfectly safe to extrapolate to 80°. The quantities of mercury in the two determinations seldom differed by as much as 0.3 gm., in which case the correction can be entirely neglected.

The altered design of the containing vessel made necessary a modification of the procedure in filling the cylinder ready for a run. The bulb was filled by boiling the liquid into it at reduced pressure at room temperature. During the filling the liquid came into contact with a gum stopper for a few seconds. The bulb was then disconnected from the air pump, and gently warmed by holding it in the hands, thus forcing a slight quantity of liquid out of the stem. After the bulb had come to the temperature of the hand, the outside was carefully wiped dry, and the stem immediately inverted into the cup of mercury. In this way the complete exclusion of all air bubbles was ensured. After the bulb had once more come to the temperature of the room, the combined weight of the filled bulb, mercury, and steel cup was found. The weight of the liquid in the bulb can then be found immediately by subtracting the known weight of the mercury, cup, and bulb. The quantity of the liquid used in the majority of the experiments was about 12 c. c. The mercury cup with the bulb still in place was now slipped over the manganin resistance coil,

[4] Bridgman, These Proceedings, **47**, 319–438 (1911).

and the coil, mercury cup, and the liquid under investigation were inserted together into the cylinder. This naturally had to be done from below, and for this purpose the cylinder was held vertical during this operation in a special vise, projecting at right angles from the wall. The packing and the retaining screw were also inserted while the cylinder was in this position. The cylinder was now filled with a weighed quantity of kerosene through the open upper end. This filling with kerosene was accomplished in two operations; first, half of the kerosene was poured in, and all air extracted from the lower part of the cylinder by gently exhausting it, and then the remainder of the kerosene was poured in. The moveable plug was then inserted, with special care not to spill any kerosene, and finally the cylinder, kept always upright, was put in position in the lower part of the press. After a run the bulb was cleaned for the next run by heating it nearly to redness. That the cleaning was thorough was shown by the constancy of weight of the bulb, which seldom varied more than one milligram from experiment to experiment.

The essential idea of the experimental method remains the same as in the work on water, but there are slight modifications. The purpose is to obtain by direct measurements the change of volume with pressure over the entire pressure range at some one constant temperature, and then by another independent set of measurements to obtain the change of volume with temperature over the entire temperature range at a sufficient number of pressures to completely cover the field. This method has a distinct advantage over that employed by Amagat, for example. Amagat obtained the volume as a function of pressure and temperature by measuring the change of volume with pressure isothermally at a number of temperatures. This has the disadvantage that the thermal dilatation can be found only by taking the difference of compressibility determinations at different temperatures. Obviously this makes it necessary to measure the compressibility with a much greater degree of accuracy than the desired final accuracy of the dilatation, and this is a difficult matter to accomplish. But the present method gives both compressibility and dilatation with the accuracy to be expected of direct measurements.

The procedure in measuring the change of volume with pressure at constant temperature was the same as in the work on water. The temperature chosen for this determination was 40°, because it is the same as was used for water. Reference is made to the former paper for the details of manipulation. In order to cover completely the pressure range, it was necessary to make the readings in two series,

one at lower pressures up to 2000 kgm., and the second between 2000 kgm. and the maximum, 12000 kgm. A similar method was found necessary in the previous work on water. The reason for this is that at high pressures the moveable piston takes a permanent set, and moves with extreme friction against the sides of the cylinder. The result is that if the pressure has once been pushed to the maximum the piston will not return far enough to reach the low pressures again. The lowest pressure that it was possible to reach after the maximum varied somewhat, but was usually in the neighborhood of 1000 kgm. In order completely to cover the field, therefore, two sets of experiments were necessary, one for the high and the other for the low pressures. To make the results comparable, the low pressure measurements were carried some distance into the high pressure domain, the upper limit of the low pressure measurements being about 2000 kgm.

The chief variation from the method of the earlier work is in finding the thermal expansion. The method of the earlier work involved two steps. The first was to change the temperature at constant volume. This change of temperature, if it were an increase, produced as a secondary effect a rise of pressure. The second step was to lower the pressure to the original value preparatory to the next change of temperature. The withdrawal of the piston necessary to effect this lowering of pressure was always attended by slight irregularities; apparently the piston does not begin its regular march until after some slight motion has taken place. So that although perfect regularity was found in the larger motions of the piston of the compressibility determinations, yet the initial irregularity was sufficient to be disturbing with the smaller motions accompanying the temperature changes. The difficulty was avoided by keeping the piston constant in position during a series of temperature changes, and allowing the pressure to vary accordingly. The variation of pressure for a change of temperature of 60°, from 20° to 80°, was about 1000 kgm. at the highest pressures, and proportionally less at the lower pressures. Temperature measurements were made at six values of the average pressure with the apparatus set up for the higher pressures, above 2000 kgm., and at two mean pressures with the apparatus set up for the lower pressures, below 2000 kgm. Readings were made at 20° intervals, as in the work on water. At 2000 kgm., for example, the temperature was raised from 20° to 40° and the increase of pressure noted, then to 60° and the increase of pressure noted again, and finally from 60° to 80° and once again the increase of pressure noted.

The pressure was then increased at 80° to the next higher value, about 3500 kgm., and the corresponding set of measurements made at 20° intervals, this time with decreasing temperature. The other four sets of readings were made in a similar way. The highest pressure reached, on the last reading at 80°, was about 12500 kgm. From here the temperature was decreased, so that the final reading at 20° was made at a pressure of about 11500 kgm. Here is an incidental advantage of the modified method of making the expansion measurements, because mercury solidifies at 20° at less than 12000 kgm., so that if the former method had been used a smaller value of the mean maximum pressure would have been necessary for the last reading at 20°. Of course the modified method necessitates a slight change in the method of making the computations, which will be described later.

All the measurements on each of the liquids were repeated to ensure greater accuracy. The measurements were made in two series; all twelve liquids were first measured, and, except for the preliminary experiments, no repetitions made until at least one set of readings had been made for each liquid. This has the advantage of separating the measurements on any one liquid by a considerable interval of time, and thereby eliminating any possible effect of temporary variations in the apparatus. During the first extended series of readings the two sets of readings for each liquid at high and low pressures were made with two separate fillings of the apparatus. At the lower pressures the viscosity effects do not play any part, so that it was not necessary to leave so large a space between the bulb and the walls of the cylinder as was necessary for the higher pressures. In this way a larger bulb could be used at the lower than at the higher pressures, so that somewhat greater sensitiveness could be obtained at the lower pressures because of the greater quantity of liquid. But this made it necessary to take the apparatus apart after the set of readings at low pressures, and replace the larger bulb by the smaller one for the run at high pressures. This made considerable trouble, which did not seem adequately compensated by the somewhat greater accuracy, so that in the repetition of the experiment the readings at the high and low pressures were all made with the same filling of the apparatus. The readings at low pressures were made before the readings at high pressures, and so before the piston had been upset.

The final detailed procedure was as follows. The readings at low pressures were made first. It is not necessary to describe them in detail as they were similar to the readings at the higher pressures, the

only difference being that no seasoning precautions were taken. At high pressures the thermostat was first adjusted to 40°, and then the cylinder seasoned over the entire pressure range by advancing the pressure to the maximum and releasing it three times. The details of the seasoning process are described in the former paper. The compressibility measurements at 40° were then made. Readings were taken both at increasing and decreasing pressures, so as to correct for hysteresis. The range of these measurements was from 2000 to 12000 kgm., returning after the complete set of readings to the initial pressure of 2000 kgm. Next, the cylinder was seasoned for the thermal expansion readings by advancing the pressure to 11500 kgm. raising the temperature to 80° at constant volume, releasing the pressure to 2000 kgm. at 80°, and finally reducing the temperature to 20°. The thermal expansion measurements were then made by the method already described.

In the later form of procedure, in which the effects at high and low pressures were measured with the same set-up, all the measurements at the low pressures and the isothermal compressibility at 40° were made on the same day; on the next day the thermal dilation at six mean pressures was measured, and the apparatus taken down and set up again with a new liquid ready for another run on the next day.

By the use of large reservoirs of hot water and by nearly emptying the thermostat at every change of temperature, it was possible to make the readings with changing temperature fairly rapidly, the elapsed time between readings at successive temperatures being about fifteen minutes. A much longer time than this would have been necessary to secure temperature equilibrium throughout the mass of the cylinder if a special device had not been adopted. This consisted in running the temperature past the final value, and then returning to it. Thus, let us suppose that the temperature was to be changed from 20° to 40°. Water was drawn from the thermostat and enough hot water poured in to raise the temperature to 45°, and not until the lapse of several minutes, the exact time to be determined by experiment, was the temperature reduced to 40° and the regulator set at this final value. After some practise it was possible to reach temperature equilibrium in little more time than was necessary for the manipulations of drawing water and putting in fresh. Readings were never made, however, until at least three minutes had elapsed without change of pressure.

The actual experiments, after the preliminary work, occupied four months, from February through May, 1912. Many of the early

measurements are due to the assistance of Mr. S. L. Gokhale. During the entire time there was no change in the internal diameter of the cylinder of so much as 0.0001 inch. To ensure further that there was no progressive change in the cylinder during the measurements, the comparison measurements with the liquid replaced by Bessemer steel were made at five intervals during this time. The maximum divergence of any of these readings from the mean was only 0.5%, better perhaps than would at first be expected from the method.

The original data are so numerous that it seemed undesirable to give them here in full. Every point recorded involves six readings, two of pressure and four of piston displacement. On the average each liquid involved 140 points, 75 for compressibility and 65 for thermal expansion. This makes a grand total of 12500 readings in the original data. It was thought to be sufficient to give a few sample curves of complete data, and to state for each liquid the average departure from the mean of the two series of compressibility and dilation measurements. The average departure from the mean of the two series of compressibility measurements for the twelve liquids was 0.15% of the maximum, and the departure from the mean of the thermal expansion measurements was 2%. The changes of volume due to changes of pressure are much greater than those due to temperature, so that the compressibility measurements determine the final accuracy of the volume.

In regard to the purity of the liquids, it was not thought necessary to take special precautions, because the properties studied here are not much influenced by the presence of impurities. The compressibility, for example, of a mixture of two liquids of small concentrations of the one in the other is an additive function of the compressibility of the two components. An example of this fact occurred in the preliminary work on ether. The first measurements were made with the ether enclosed in a glass bulb. This bulb broke on the application of pressure because of the great viscosity of the kerosene. The compressibility measurements of this preliminary run were measurements, therefore, on a mixture of ether and kerosene. In spite of the fact that this ether was very much contaminated the result showed that the compressibility of this mixture was only different by 4% from what it was when the measurements were made on the same quantities of ether and kerosene prevented from mixing.

The liquids used were obtained from Eimer and Amend. They were either the purest manufactured by them, or else Kahlbaum's purest. It was to be expected therefore, that only slight impurities

were present, and that the errors due to them are beyond the limits of observational error.

Nine months after the completion of the experiments, the remaining samples were subjected to a rough analysis by determining the boiling points. If the liquid is pure, the boiling point should remain constant until the liquid is completely boiled away. The amount by which the boiling point changes during evaporation can be expected to give at least some clue as to the amount of impurity present. [A substance is considered good enough for most *chemical* purposes if it all boils within 1°.] Of course this analysis does not give the nature of the impurity present, nor does it give the impurity at the time the experiment was performed. During the nine months the liquids were left tightly corked, but there can be no question that some deterioration had gone on in this time, so that the liquids were all actually better than is indicated by the analyses. The deterioration with time is much greater for some liquids than for others.

The fractionations were performed by Mr. R. H. Patch at the Chemical Laboratory of Harvard University. The results of his examination are given below. It should be noticed that the temperature readings have not been corrected, so that all they can show is the constancy of the boiling point, not its absolute value.

Methyl Alcohol (*Kahlbaum*).

93% boils between 64.5° and 65° C.
7% " " 65° and 65.8° C.

Free from ethyl alcohol and acetone, the most likely impurities, and was neutral to litmus. Excellent sample. (It would seem that the impurity was probably water, most of which had probably been absorbed while standing, as the stopper was not perfectly tight).

Ethyl Alcohol (*Kahlbaum*).

3.8% boils between 77.3° and 77.8° C.
96.2% " " 77.8° and 78.0° C.

The sample showed some suspended inorganic matter, probably iron from the container. (The sample had been standing for the nine months tightly corked with a cork stopper in the tin vessel in which it came from Kahlbaum). With this exception, and admitting the presence of a small quantity of water the sample was a good one.

Propyl Alcohol (*Kahlbaum*).

4.% boils below 96.° C.
96.% boils between 96.0° and 96.8° C.

A good sample.

Isobutyl Alcohol (Eimer and Amend).

7% boils below 105.8° C.
17% boils between 105.8° and 107° C.
76% " " 107.0° and 107.2° C.
Thus 93% boils within 1.4°, a good sample.

Amyl Alcohol (*Kahlbaum, Free from Pyridin*).

3% boils below 128.9° C.
89.5% boils between 128.9° and 129.9° C.
7.5 boils between 129.9° and 130.0° C.
Sample free from foreign organic matter and neutral to litmus. An excellent example.

Ethyl Ether (*Kahlbaum, "Sp. gr. 0.720"*).

The whole sample boiled between 34.5° and 35.0° C.
Neutral to litmus, free from aldehydes, and sulphur compounds.
Contained some water, and without doubt some alcohol.

Acetone (*Eimer and Amend. Marked "Pure"*).

70.6% boils between 56° and 57° C.
19.4% boils between 57° and 58° C.
10% boils between 58° and 59° C.
The sample left a dark brown residue in the distillation flask, probably aldehydic in nature. Free from water, and neutral to litmus. A fair sample. (The brown color developed on standing; at the time the experiment was performed, the liquid was perfectly colorless.)

Carbon Bisulphide (*From the store room of the Chemical Laboratory*).

5% boils between 45.8° and 46.° C.
95 boils at 46.0° C.
The sample was free from hydrogen sulphide, sulphuric and sulphurous acids, but contains some foreign organic sulphur compounds and left a yellowish residue. The latter always results upon allowing the liquid to stand, especially upon exposure to light. (Here again the color had developed upon standing during the nine months. At the time of the experiment the liquid was perfectly colorless.)

Phosphorus Trichloride (*Eimer and Amend*).

True boiling point is 78.3° C.
Sample showed no constant boiling point.
6.5° boiled below 77° C.
11.2% boiled between 77° and 79° C.
17.9% boiled between 79° and 80° C.

15.9% boiled between 80° and 81° C.
17.9% boiled between 81° and 87° C.
31.4% boiled between 87° and 102° C.
Chief impurity probably phosphorus oxychloride formed by combination of the trichloride with the moisture in the air, also some pentachloride is almost always unavoidably present, due to excess chlorine.

Ethyl Bromide (Eimer and Amend).

The whole sample boiled from 38.0° to 38.4° C. and with the exception of not over 2% at 38.4° exactly. Neutral to litmus, an excellent sample.

Analyses could not be made of the ethyl chloride and the ethyl iodide, because these samples were completely used up in the experiment. Both of these were obtained in sealed glass bulbs from Kahlbaum, were used immediately after opening, and were both colorless when used.

These analyses show that probably none of the liquids contained enough impurity to have any perceptible effect, except the phosphorus trichloride, and to a less degree the acetone. The phosphorus trichloride was very noticeably simpler in its behavior at high pressures than the other liquids; probably due to the fact that it is a mixture of different substances, and so can not be expected to show the well marked behavior of a single pure substance.

A few measurements were made on one liquid which are not tabulated here. These were measurements on chloroform, which was found to freeze at fairly low pressures, about 6800 kgm. at 40°, and 10000 kgm. at 80°. Further investigation of this liquid has been postponed until a systematic investigation of freezing curves can be taken up.

III. Methods of Computation.

The methods of computation were slightly different from those used in the work on water, in part because of the somewhat different experimental method. They are, in consequence, here described in detail. As in the computations for water, the first step was to prepare a table giving the volume at regular intervals of pressure and temperature. From this table the other thermodynamic quantities were then computed.

The Table of Volumes. In preparing the table of volumes, the first computation was of the volume as a function of pressure at 40°. The first step was to plot the piston displacement against the displacement

of the slider of the bridge wire on which the resistance of the manganin coil was measured. Because of hysteresis effects it was necessary to make two sets of readings, one with increasing and the other with decreasing pressure. Care was taken that any two corresponding readings should be at as nearly as possible the same pressure, so that it should be allowable to take the average of two corresponding displacements as the best value of the displacement at the average of the two corresponding pressures. The next step was to draw a smooth curve through the average points, and from the curve to tabulate the displacement at regular intervals of pressures (5 cm. on the bridge wire, or about 1100 kgm.). The second series of measurements on the same liquid was then treated in the same way. These two series of measurements differed somewhat as to the quantities of materials used, that is, the liquid under investigation, the kerosene, the mercury, and the steel. But the amounts were so nearly the same that it was permissible to take the average displacement of the two series as the displacement that would have been found for the mean between the quantities of material used in the two series. In only a few cases did the amounts of material in the two series differ so much that it was not permissible to do this. In these cases the displacement for the mean quantity had to be determined in a way which need not be described in detail. The average of the displacements obtained in this way were now corrected for the effect of the kerosene, the mercury, the steel, and the distortion of the steel containing vessel. In applying the corrections, the mean of the five auxiliary experiments in which the liquid was replaced by Bessemer steel was used. The correction was applied in essentially the same way as for water. The corrected result gave the motion of the piston due to the compression of only the liquid under investigation. This, with the known cross section of the piston and the weight of the liquid, determined the change of volume at any pressure of 1 gm. of the liquid. Finally, by using the values for the density at 0° deduced from the recent Tables of Kaye and Laby, the results were reduced to the change of volume in c. c. of a quantity of liquid which at 0° C. and atmospheric pressure occupies 1 c. c. This is the unit quantity which is here adopted throughout, and seems to have been most usually used in work of this kind. In particular it is the unit quantity of Amagat.

The computation just described applies only to the measurements at the higher pressures. The results are tabulated as changes of volume from 2000 kgm. as the zero of pressure. If the pressure during the high pressure measurements went lower than this, as it usually did,

the corresponding changes of volume were taken as negative. To obtain the volume at lower pressures, the measurements at the lower pressures were reduced in much the same way as has been described for the higher pressures. One difference is that the measurements at the lower pressures were at 20° instead of 40°, because several of the liquids boil at less than 40° at atmospheric pressure. It was not possible to reach entirely to the zero of pressure with the low-pressure measurements, because of the slight friction of the piston even when the pressure had not been pushed so high as to permanently upset the piston. It was not possible to get much nearer to zero than 100 or 200 kgm. after the pressure had once been pushed to 2000 kgm. In order to come still closer to zero, several measurements were made during the very first application of pressure, before the cylinder has been seasoned for hysteresis. During these first readings the pressure was increased to about 1000 kgm. and then seasoned for hysteresis as before. As a result the second set of readings between 200 and 2000 kgm. made after this seasoning process did not make close connection with the first set. The discrepancy was due in part to hysteresis, but also in part to better adaptation of the packing to all the crevices in the steel washers. The direction of the two curves was usually the same, however, within the limits of error. This allowed an extrapolation to zero by combining the results of the first set of readings with those of the second. In this way the change of the unit volume from atmospheric pressure up to 2000 kgm. was determined. It must be remembered, however, that the readings at the very lowest pressures are almost certainly in error, because the instrument is not designed for low pressures. But with increasing pressure the readings become more and more trustworthy, until above 500 kgm. they seem to merit entire confidence, if we can judge from self consistency. To get the total change of volume from atmospheric pressure it is desirable, therefore, to supplement these readings with others made with apparatus especially designed for low pressures. Such measurements are afforded by the data of Amagat, and in some cases by others.

At the time that the computations of this paper were made, the data of Amagat were the best that we had for the compressibility at low pressures. Between the time of computing these results and writing this account, however, there has appeared a paper by Richards,[5] in which the compressibility up to 500 kgm. of several of the liquids

[5] Richards, Jour. Amer. Chem. Soc., **34**, 971–993 (1912).

used here is determined. It is unfortunate that these values did not appear in time for use in the present computations. They are quoted, however, so as to afford a comparison with the results of Amagat, which are here used as the standard for low pressures. It makes no difference with the essential conclusions of the paper, however, which set of data is accepted as most probably correct. The only effect would be to change the initial values of some of the thermodynamic properties; their magnitudes at high pressures will not be altered.

The precise steps in combining into a final result the changes of volume computed from the two sets of readings at high and low pressures were as follows. From the high pressure readings, the changes of volume at 40° (ΔV, cm.^{3}/cm.^{3}) were plotted against the displacement of the slider of the resistance bridge, the zero of pressure being at 10 cm. displacement. The scale of the diagram was large; 2 cm. for 0.1 inch piston displacement, and 55 cm. slider displacement for the maximum pressure. From the low pressure readings ΔV in cm.^{3}/cm.^{3} was found at 20°, and was plotted against slider displacement, the zero being at 5 cm. A smooth curve was drawn through these points. From this curve, knowing the constants of the manganin coil, ΔV was found at 500, 1000, 1500, and 2000 kgm. and 500, 1000, 1500, and 2000 atmos. ΔV in terms of atmos. was now corrected so as to be reckoned from 1000 atmos. as zero. The values of Amagat for ΔV at 20° were next computed with 1000 atmos. as the zero. These two sets of data were compared, and the new values for the lowest interval adjusted so as to be in agreement with Amagat between 1 and 500 kgm. It will be noticed that this preliminary comparison with Amagat does not enter the final result; it was an orienting comparison for obtaining some idea of the accuracy at low pressures. Using Amagat's value for the lower interval, the changes of volume at pressures corresponding to 2.5, 5.0, 7.5, and 10.0 cm. were next determined, reckoned from zero pressure. These values were now corrected to 40° with the data obtained for the thermal dilatation and were recomputed with 10 cm. as the zero of pressure. The changes of volume at 40° obtained from both the low and high pressure sets of measurements were now plotted together on one diagram, and a smooth curve drawn through the points. From this curve the changes of volume with the kilogram as the unit of pressure were read off at 500 kgm. intervals, starting from an origin at 500 kgm. The changes of volume so found were now smoothed to give regular differences. The smoothing was performed in a manner somewhat different from

the corresponding operation for water, and in a manner which has the advantage of preserving the irregularities which are shown by experiment actually to exist, but which would have been effaced if the attempt were made to give smooth second differences, as was done for water. In performing this smoothing, the fact was used that the change of volume of nearly all the liquids can be represented by a curve of nearly the same shape. Ethyl chloride is an exception, and a special computation had to be applied to it. As a first approximation the change of volume of the other eleven liquids was found to be reproducible by a formula of the type;

$$\Delta V = \alpha\left(\frac{p-500}{1000}\right)^{.8} + \beta\left(\frac{p-500}{1000}\right)^{.6} + \gamma\left(\frac{p-500}{1000}\right)^{.4} + \delta\left(\frac{p-500}{1000}\right)^{.2}.$$

In order to apply this formula to any one liquid it is necessary simply to multiply all four constants by the same factor. The meaning of this is that to this degree of approximation the chief difference of the liquids with regard to changes of volume is in respect to the absolute, not the relative magnitudes of the change. The constants of the above formula were computed, therefore, so as to apply to the average of the eleven liquids. This was done by finding the average change of volume for the eleven liquids at 1500, 3000, 7000, and 12000 kgm. and determining the four constants of the formula so that the curve should pass through these four points. It will be noticed that in this formula the zero of pressure is at 500 kgm., so that it applies directly to the changes of volume as found above. The formula was now applied to the eleven liquids in succession by multiplying the four constants by the appropriate multiplier for each liquid. The multiplier was so determined that the formula should give the observed change of volume at 7000 kgm. The changes of volume were now calculated with this formula at intervals of 500 kgm. up to 5000 kgm., and beyond 5000 kgm. at intervals of 1000 kgm., and compared with the observed values. The differences between the observed and the computed values were plotted on a large scale and a smooth curve drawn through the points. The values obtained from these smooth curves and the formula were combined to give the final values for the volume at 40°. The advantage of the method is that the final results lie on perfectly smooth curves, and that the curves show the various slight irregularities which correspond to the experimental facts but which would be smoothed out if the second differences were made uniform. The values for ethyl chloride were

treated in the same way, except that it was necessary to start from a slightly different formula, to be given on page 67.

It would have been possible to dispense with this finer adjustment by means of a difference curve with very little change in the final result, because the changes of volume obtained from the original

TABLE I.

METHYL ALCOHOL.

DIFFERENCE BETWEEN VOLUME OBTAINED FROM ORIGINAL SMOOTH CURVE AND FINAL COMPUTED VALUE.

Pressure. $\frac{\text{kgm.}}{\text{cm.}^2}$	Difference.	Pressure. $\frac{\text{kgm.}}{\text{cm.}^2}$	Difference.
500	.0000	5000	−3
1000	−.0000	6000	+2
1500	−1	7000	−3
2000	0	8000	−1
2500	−1	9000	0
3000	+1	10000	0
3500	−2	11000	−1
4000	+1	12000	0
4500	0		

smooth curves were almost the same as given by the final computation. Table I shows for one liquid (methyl alcohol, chosen at random) the very slight changes made by this readjustment.

The values obtained by this computation start from 500 kgm. as the zero. The change of volume between atmospheric pressure and 500 kgm. has been taken directly from the results of Amagat in those cases where his data are sufficient. In some cases where Amagat does not give the data, it has been necessary to use the more inaccurate values of the present method. In the detailed presentation of data for each liquid, the values taken from Amagat are given. If it should happen at any future time that more probable values than these of

Amagat are found for the changes of volume at low pressures (which indeed is already the case for those liquids measured by Richards), then the results given here may be corrected by adding a constant to the volumes throughout the tables, except of course at atmospheric pressure. The addition of such a constant to the volumes will not alter the behavior of any of the thermodynamic properties at high pressures; it can at most affect those which involve integrations by a very small constant corrective term.

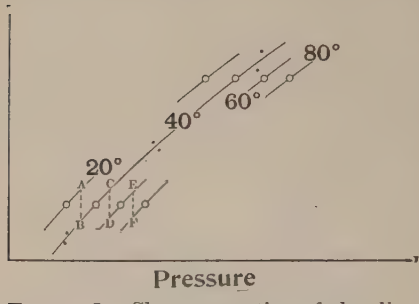

FIGURE 2. Shows a portion of the diagram for determining the compressibility and thermal expansion from the piston displacements. The piston displacements are plotted against pressure. The heavy points are the readings with increasing and decreasing pressure at 40° for the isothermal compressibility. The discrepancy between these points is due to hysteresis. The open circles show the readings at constant volume with changing temperature. The dotted lines, *AB* for example, show the piston displacement which would have been found if the temperature had been changed at constant pressure.

That it was possible to represent the approximate behavior of these twelve liquids by similar formulas is itself a somewhat surprising and significant fact. It seems to suggest that at extremely high pressures all liquids become alike. The greatest differences between different liquids are at the low pressures. The use of a separate formula in the case of ethyl chloride, which might appear to be an exception, was necessitated in fact only by its abnormal compressibility at low pressures.

It was necessary to compute the thermal dilatation also by a method slightly different from that used for water, because only one piston displacement was read at each temperature instead of two. The piston displacements were plotted against pressure on the same diagram as the isothermal compressibility at 40°. (See Figure 2.) Through each of the points a curve was drawn of the same general slope as the curve of pressure and volume at 40°. The slight changes necessary in the slope of this curve at different temperatures could be made graphically with sufficient accuracy. The difference of the piston displacement for every interval of 20° at the mean of the two pressures involved was now read from these curves. Thus in Figure 2, the line AB represents the piston displacement at constant pressure

corresponding to a rise of temperature from 20° to 40°, CD from 40° to 60°, and EF from 60° to 80°. These displacements correspond to slightly different values of the mean pressure. The piston displacements at constant pressure obtained from a diagram like Figure 2 were then plotted against pressure on another diagram, the points for the two independent series of measurements on the same liquid being plotted on the same sheet. The quantities of liquid used in the two series were usually so nearly the same that the mean of the piston displacements could be assumed without error to be the piston displacement of the mean quantity of liquid. The mean of the two independent series of readings was found graphically from the diagram by drawing a smooth curve through the two sets of points. From this value of the piston displacement, after corrections had been applied for the kerosene, mercury, and steel, the change of volume per unit quantity for intervals of 20° was computed in a way analogous to the similar computations for the compressibility. Here again the values for the low pressures are most likely to be in error. The change of volume at 20° intervals at atmospheric pressure was taken directly from the tables of Landolt and Börnstein. Finally, the experimental points and the points at atmospheric pressure were plotted together on a single diagram, smooth curves drawn through them, and from these curves the changes of volume for intervals of 20° were obtained which were used in the construction of the tables of volume.

In plotting as above on a single diagram ΔV for 20° intervals, two independent series of measurements, namely those of this paper and those on which the formulas of Landolt and Börnstein are based were therefore brought together. The two sets of data should of course, if consistent, lie on a smooth curve, so that the amount of discrepancy might be expected to afford an indication of the order of accuracy at low pressures. The change in the dilatation is, however, so rapid at the low pressures that it was possible in nearly every instance to make smooth connection between the two sets of points, without departing from either of them. Furthermore, it would be possible in most cases to make just as smooth connection if somewhat different values were used at atmospheric pressure. Slight discrepancies between the smooth curves and the individual points do not therefore, give a reliable indication of the accuracy.

The thermal dilatation is probably not so accurate as are the changes of volume with pressure, because the dilatation is much smaller. The dilatation can be measured with no greater accuracy than the changes of pressure accompanying the changes of temperature at constant

volume. These changes were of the order of 200 kgm. for 20° intervals and could be read on the bridge with an accuracy of about $\frac{2}{3}\%$. The agreement between the two independent sets of readings was not in general as good as this, averaging about 2%. This is better than was expected at first could be obtained with the method, and is certainly

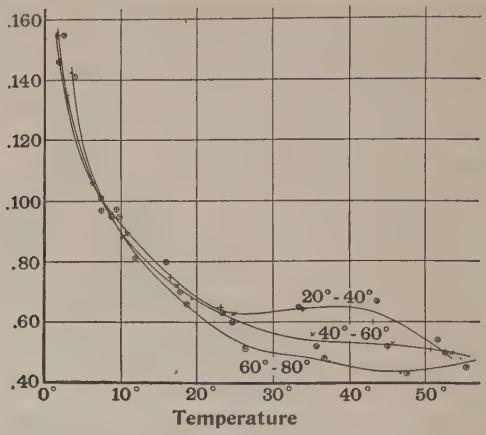

FIGURE 3. A sample set of observations on the change of volume with temperature at constant pressure. The ordinates are piston displacements in inches. Two independent sets of readings are shown on the diagram, those with the circles are the repeated set. The liquid shown here is carbon bisulphide. The accuracy for this is almost exactly the average accuracy for all twelve liquids.

much better than could have been obtained with the alternative method of determining the difference between isothermal lines for different temperatures. Figure 3 for carbon bisulphide shows a fair average of the order of agreement. A more detailed account of the order of accuracy will be given under the description of the individual liquids.

The material was now at hand for the construction of the table of volumes. Up to 5000 kgm. the volume was to be tabulated at intervals of 500 kgm., and above 5000 kgm. at intervals of 1000 kgm. The difference in the length of the pressure steps is desirable because at low pressures the volume changes more rapidly than at high pressures. The tabulation at each pressure was to be made at temperature intervals of 10°. The volume as a function of temperature at atmospheric pressure was first tabulated. This was taken from the formulas of Landolt and Börnstein, or from other sources to be described in detail under the separate liquids. The agreement between different observers, even for atmospheric pressure, is not always as close as could be

desired. The next step was to tabulate the volume as a function of pressure over the entire pressure range at 40°, starting from the volume at atmospheric pressure and 40°. These values were then combined with the change of volume for 20° intervals, thus giving the volume for each pressure at 20°, 60° and 80°. To obtain the volume at the intermediate intervals of 10° a device was adopted which at the same time gave the material for determining the thermal dilatation. The change of volume to be expected at 40° and 60° if the change had been linear with temperature over the entire range was calculated from the total change of volume between 20° and 80°. The differences between the actual and the calculated changes of volume were plotted against temperature for each pressure of the table, and smooth curves drawn through these points. From these curves the departure from linearity at the intermediate intervals of 10° was found, and combined with the values computed by the linear relation to give the total change of volume at the desired 10° intervals. This method, as the method for computing the isothermal compressibility, has the advantage of giving smooth curves without smoothing off the second differences.

Thermal Dilatation.—From the table of volumes the next problem was to compute the more significant quantities of thermodynamic interest. The first of these was the thermal dilatation, or $\left(\frac{\partial v}{\partial \tau}\right)_p$. "Dilatation" is perhaps not generally used in this sense, $\frac{1}{v}\left(\frac{\partial v}{\partial \tau}\right)_p$ being more common, but it has the advantage of being the quantity which enters directly into the thermodynamic formulas. The quantity of material to which the former differentiation refers is the unit used throughout this paper, namely the quantity which at 0°C. and atmospheric pressure occupies 1 c.c.

Evidently if the dilatation were uniform over the entire temperature range it could be found from the change of volume between 20° and 80° by dividing by 60. The dilatation is not linear, however, but departs from linearity in a way which can be found from the curves used to determine the change of volume at 10° intervals. The correction to the linear value is obviously to be found from the slope of the difference curve, which can be found graphically from a large drawing with sufficient accuracy. The dilatation was determined in this way at 20° intervals, and was plotted as a function of the pressure for each of the twelve liquids.

The details of the computations for the volume at 10° intervals and of the dilatation are shown more clearly perhaps in Figures 4

and 5. The experimental values of the changes of volume at 20° intervals were first plotted. A represents the change from 20° to 40°, B the change from 20° to 60° (obtained by adding the change 40°–60° to the change 20°–40°) and C the change 20° to 80°. The origin was now connected to C by a straight line (this was done actually by a compu-

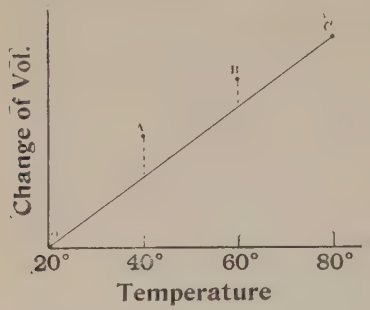

FIGURE 4. Shows the first step in finding the change of volume at intervals of 10° and the thermal expansion from the readings of the volumes at 20° intervals. The heavy line shows what the volume would be if the relation between volume and temperature were linear.

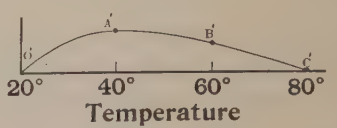

FIGURE 5. Second step in finding change of volume at 10° intervals and the thermal expansion. The point A' is the difference between the point A of Figure 4 and the straight line. The ordinates of this curve at intermediate points, when added to the ordinates given by the straight line of Figure 4 at corresponding points, give the volume at intermediate points. The slope at A' when added to the slope of the straight line of Figure 4, gives the thermal expansion at 40°, for example.

tation, not graphically) and the differences between the points 0, A, B, and C and this straight line were plotted on another diagram, Figure 5, on a larger scale. A smooth curve was drawn through these four points; from this curve the ordinates were read at the intermediate intervals of 10°, and combined with the straight line values of Figure 4 to give the volume at the temperature in question. The thermal dilatation at any temperature, 40° for example, was found by adding to the slope of the straight line 0C the slope determined graphically at the point A′ of Figure 5.

This method was also applied in determining the dilatation at atmospheric pressure. An alternative method would have been by differentiating the power series of Landolt and Börnstein for volume as a function of temperature. The graphical method was thought preferable, however, because a power series may often reproduce the experimental points with greater fidelity than the slope of the experimental curve.

The dilatation, computed in this way, was transferred directly to tables, and from the tables the curves were drawn which are given later

for the dilatation. In order to save space, these tables are not given here. The thermal dilatation enters into many of the other thermodynamic quantities listed in this paper. In computing these quantities the values of the dilatation given in the tables have been used, not the values obtained from the curves given later. The same is true for all the other thermodynamic properties listed in the paper; tables were first computed for all of them before curves had been drawn for any. In this way any progressive error was avoided which might have been introduced by the use of diagrams. Although each diagram shows the property in question with as great an accuracy as is justified experimentally, it might be that if a computation involved the transference of points from one diagram to another several times, the error so introduced might finally mount up to more than the experimental error.

Isothermal Compressibility. — The compressibility, or the quantity $\left(\frac{\partial v}{\partial p}\right)_\tau$, was the next to be determined. This was found by a method somewhat analogous to that for the dilatation. Evidently the compressibility does not vary greatly with temperature. If the compressibility can be found as a function of pressure for one constant temperature, then the compressibility at other temperatures can be found by applying a small correction. The temperature chosen for the direct determination of the compressibility was 40°, since this was the temperature at which the change of volume with pressure had been found. The compressibility was determined graphically from a large scale drawing of the change of volume against pressure. An alternative method would have been to calculate mathematically the slope from the approximate formula for the change of volume, and then to correct this by the graphically determined slope of the difference curve. But this method would fail at the lowest pressure, 500 kgm., and at the higher pressures it did not prove necessary, because the simpler direct graphical method was sufficiently accurate.

It was now possible to correct the compressibility at 40° to the other temperatures of the tables by the use of difference curves. Let us suppose that it was desired to find the compressibility at 60°. Figure 6 represents graphically the operation which was actually performed by a computation. The curve of volume at 60° against pressure was displaced downwards (shown in the dotted line) so as to have the same origin as the curve for 40°. The difference between the curves was plotted on a large scale against pressure, and the graphically determined slope of the difference curve used as a cor-

rection to bring the compressibility from 40° to 60°. The process was performed for intervals of 20°, and the results were tabulated and plotted for the twelve liquids.

The compressibility is most likely to be in error at the lower pressures, as was the dilatation. In particular, the compressibility at atmospheric pressure can be found from the method outlined above only by a wide extrapolation, and therefore is not accurate. Another method was adopted, therefore, at atmospheric pressure. Of course, the compressibilities ought to be consistent with the tables of volumes, that is, it ought to be possible to compute from the compressibility to the change of volume given in the table. The compressibility at atmospheric pressure was accordingly computed so that when combined with the compressibility at 500 kgm. it should give the proper change of volume between atmospheric pressure and 500 kgm. It was assumed in the computation that the mean compressibility between 1 and 500 kgm. was the average of the compressibilities at 1 and 500 kgm. This is not quite true, because the compressibility varies rapidly with pressure at low pressures. The value computed in this way is likely to be somewhat low. The discrepancy cannot be large, however, and this method was accepted as the best under the circumstances. The compressibility at atmospheric pressure has also been determined in a number of instances by other observers. There is not always, however, very good agreement between other observers even at atmospheric pressure, so that the compressibility at atmospheric pressure might well be the subject for further experiment in some cases. The actual disagreement at atmospheric pressure and the probable accuracy of the value finally chosen is to be given in the detailed discussion for the separate liquids.

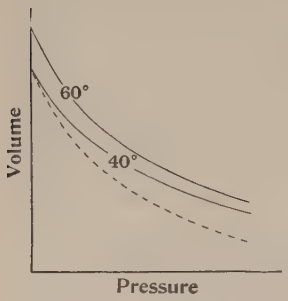

FIGURE 6. Illustrates the method for finding the temperature correction of the compressibility.

The Work of Compression. — The mechanical work of compression was the next quantity of thermodynamic interest to be computed. This is given by the formula $\left(\frac{\partial W}{\partial p}\right)_\tau = -p\left(\frac{\partial v}{\partial p}\right)_\tau$. To find the total quantity of work done from zero up to any given pressure it is evidently necessary to integrate the derivative. This integration was performed mechanically with the integraph of the mathematical

department of Harvard University. In performing the integration there are two possible methods. We may either integrate $p\left(\frac{\partial v}{\partial p}\right)_\tau$ as given above, or we may integrate the equivalent expression $\left(\frac{\partial W}{\partial v}\right)_\tau = p$. The first involves an integration with pressure as the independent variable, and the second with volume. The first uses as the integrand the compressibility, which was obtained by computation from the experimental data, and the second uses as the integrand the pressure, which is one of the direct experimental data. It is well known that the derivative of an experimental quantity has considerably greater error than the experimental quantity itself. The second method was adopted, therefore, using the volume as the independent variable of integration. It was a fortunate accident that the method could be used without duplication of effort, because the volume had already been plotted against pressure for another purpose. However, the direct results of the integration were not immediately available because it was necessary to obtain the work of compression as a function of pressure instead of as a function of volume. The change of variable was made with the help of the curves of volume against pressure by reading off the pressures corresponding to the given volumes.

The work of compression was found by the method outlined above at 20° intervals of temperature. It differs only slightly for different temperatures, so slightly that the difference of the work at different temperatures could not be obtained directly from the curves with as great accuracy as was necessary for computing the specific heats. In order to obtain the differences of the work with greater accuracy, an independent integration of the quantity $\Delta p\left(\frac{\partial v}{\partial p}\right)_\tau dp$ was performed. The symbol Δ indicates the difference of the product $p\left(\frac{\partial v}{\partial p}\right)_\tau$ at a given pressure for the interval 20°–40° or 40°–60° or 60°–80. These differences were taken from the tables of compressibility. The integration of the differences was performed with the integrating machine. Tests of the integrating machine showed that the accuracy of this part of the process alone was as high as $\frac{1}{10}$ %. The differences found in this way were now used in finding a better mean value for the total work of isothermal compression. For it is evidently possible with these differences to correct the work of compression at 20° or 60° or 80° back to 40°. If there were no error all these values should

agree, but of course complete agreement could not be expected. The agreement of the values corrected to 40° in this way was a few tenths of a per cent. The final value at 40° was taken as the mean of the four corrected values, and is shown in the diagrams. In the lower part of the diagrams the relation between pressure and the difference of the work of compression for 20° intervals is plotted on a larger scale.

The Heat of Compression.— The heat of compression was the next quantity to be computed. It is unfortunate that the expression, "heat of compression" is sometimes used in a sense which is not indicated by the words themselves; namely, as the rise of temperature when the pressure on a substance is increased adiabatically by the unit amount. But by no stretch of the imagination is it possible to identify a temperature with a "heat." A more descriptive name for this effect would seem to be the "temperature effect of compression." The effect was discussed under this name in the previous paper on water. By "heat of compression" we shall mean in this paper what is naturally suggested by the words, namely the heat, Q, which is given out by a unit quantity of a substance when it is compressed isothermally. It may be computed if the dilatation is known, by using the formula $\left(\frac{\partial Q}{\partial p}\right)_\tau = \tau\left(\frac{\partial v}{\partial \tau}\right)_p$. To find the total heat given out by the substance as it is compressed from the initial to the final state it is necessary to integrate this expression. The procedure was exactly analogous to that in computing the work of compression. The integration was performed first for the four temperatures. Then, in order to obtain the differences more accurately, a separate integration was made of the differences of $\tau\left(\frac{\partial v}{\partial \tau}\right)_p$ for intervals of temperature of 20°. With these differences the total heat at any temperature was corrected to 40°, thus giving four values for the heat of compression at 40°, of which the mean was taken for the final value at this temperature. From this final value, the values for the other temperatures were found by computing back again with the differences. The magnitude of the differences is much greater than the differences of the mechanical work, so that it was possible to plot the total heat for each temperature without confusing the diagram.

Change of Internal Energy.— From the heat of compression and the mechanical work of compression we may find at once the change of internal energy when the liquid is compressed isothermally. During compression the liquid receives work from the compressing force and delivers heat. The change of internal energy is the difference

between the work received and the heat given out. It was computed in this way and is given in a set of diagrams (Folder 5) for the four regular temperature intervals.

Specific Heat at Constant Pressure.— Other thermodynamic quantities of a simple nature which are usually thought of as characteristic of a liquid are its two specific heats. They also may be found by thermodynamic computation from the data given, but the accuracy is not so great as the accuracy of the other quantities. There are two methods of attack open to us here, but both of them must assume as known the specific heats at atmospheric pressure as a function of temperature. In general, it may be shown that the characteristic equation of a substance is not sufficient in itself to determine the specific heats; we must know in addition the specific heats along some line not an isothermal. Unfortunately, the specific heat of very few of the liquids with which we are concerned is known with accuracy as a function of temperature at atmospheric pressure. The results of different observers are often in essential disagreement. But the characteristic equation can give us the *change* of specific heats along an isothermal. These are the results which will be tabulated in this paper, therefore, leaving for other experimenters the more accurate determination of the specific heats at atmospheric pressure. These future results may then be combined with the differences given here to determine the specific heat at any pressure.

The first method for calculating the specific heat at constant pressure is the method used in the paper on water. It makes use of the formula $\left(\frac{\partial C_p}{\partial p}\right)_\tau = -\tau\left(\frac{\partial^2 v}{\partial \tau^2}\right)_p$. Evidently in order to obtain the total change of specific heat at any pressure we must perform an integration. The weakness of the method is that it involves the use of a second derivative, which cannot be determined with great accuracy from measurements of volume. The method would be open to greater error if applied to these twelve liquids than in the case of water, because the dilatation varies more and more irregularly than for water.

The second method uses a cyclic process to determine the amount of heat absorbed in passing from one temperature to another at any constant pressure. Let us imagine a liquid in the condition represented by the point A on the diagram (see Figure 7). The liquid is now to be carried to the neighboring point D at the same pressure but at a higher temperature. The total change of internal energy when we arrive at D is independent of the path which we have tra-

versed. One path from A to D may be described by raising the temperature from t_0 to t_1 at constant pressure. (Path AD in Figure 7.) In this case the liquid does a certain amount of mechanical work against external pressure and also absorbs a quantity of heat which we can compute immediately when we know the specific heat at constant pressure. The external work during this process is simply the product of the constant pressure and the change of volume, and may be computed directly from the table of volume as a function of pressure and temperature. Or we may pass from A to D by a more circuitous route, by lowering the pressure isothermally at t_0 from A to B, then raising the temperature at atmospheric pressure from B to C, and then increasing the pressure isothermally at the final temperature t_1 to the point D. Now the advantage of this longer route is that we know all the quantities of energy which enter the body on the way. The mechanical work of compression along the isothermals from A to B and from C to D we have already computed. We have also found the heat of compression along the lines A–B and C–B. No work is done in the expansion along the line B–C, and the heat absorbed along this line is known if we know the specific heat at atmospheric pressure. By comparing the inflow of energy along these different paths we are in a position to compute either the quantity of heat absorbed along the line A–D at constant pressure, or else the difference between this heat and the heat absorbed along the line B–C. This heat (or else the difference of heat) may be plotted against the difference of temperature between the points A and D. The same process may be performed at the same pressure for a number of temperature intervals, each with t_0 as the lower limit, giving a curve of the quantity of heat absorbed at constant pressure as a function of the temperature. The specific heat at any temperature is the slope of this heat curve at that temperature.

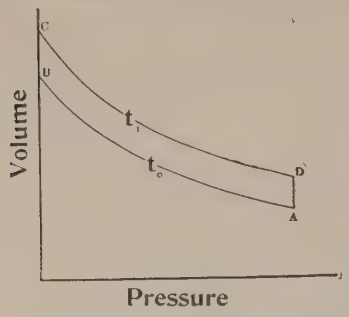

FIGURE 7. Shows the cycles described in finding the specific heat at constant pressure.

The slope was found by a method similar to that for computing the thermal dilatation at constant pressure. At any temperature the difference between the amount of heat actually absorbed and the amount which would have been absorbed if the relation between heat

and temperature had been linear was computed and plotted against temperature. The slope of the difference curve was then found graphically, and applied as a correction to the value found on the assumption of a linear relation. The modification if C_p at atmospheric pressure is not known is obvious; a similar procedure, plotting now the difference of heats against temperature gives the difference of the specific heats at the pressure in question and atmospheric pressure. In a few cases, where the liquid boiled at a low temperature at atmospheric pressure so that it was not possible to prolong the curves to the origin of pressure, the difference between the specific heats at the pressure in question and 500 or 1000 kgm. has been given.

It is now obvious why it was necessary to know the differences of the mechanical work and the heat of compression at different temperatures with a greater accuracy than could be found from the curves obtained by a direct integration.

The units in which the specific heats are given should perhaps be mentioned because they are unusual. It is customary to give the specific heat in gm. cal. per gm. of the liquid. But this method of measuring specific heat makes no connection with the thermodynamic formulas, in which the heat is measured in mechanical units corresponding to the units of the other quantities. It was preferred here, therefore, to give the heat in units which are more unusual, but which are consistent with the other quantities, so that it is possible to substitute any of the quantities directly in the formulas without the troublesome work of changing the units. The unit of pressure is the kgm. per sq. cm., and the unit of volume the c.c. Therefore the unit of work which fits the formulas is the kgm. cm., and this is the unit in which the results have been tabulated. It is to be noticed that in making comparison with the usual values of the specific heats, it is not only necessary to change the unit of work, but the unit of quantity as well, because the amount of liquid to which this value of the specific heat is referred is not the gm., as is usual, but is the amount of liquid which at 0° C and atmospheric pressure occupies 1 c.c. In order to convert the usual value of the specific heat into these units, it is necessary to multiply by the density of the liquid at 0° and atmospheric pressure, and by 42.66, the number of kgm. cm. in 1 gm. cal.

As a check on the specific heat at constant pressure found in this way, the same quantity was computed for the first three alcohols, that is for methyl, ethyl, and propyl alcohol, by the alternative method involving the second temperature derivative of the volume which was used in the paper on water. The second derivatives were found

graphically from the curves of dilatation against temperature at constant pressure, and were integrated mechanically. The results so found agree fairly well with the values found by the other more accurate method. The magnitude of the discrepancies might be as much as 10%, but all the essential characteristics of the curve as given by one method were reproduced by the other also, such as the maxima and the minima, and the points of inflection. Of course the pressure of maximum or minimum was sometimes displaced, as was to be expected.

Specific Heat at Constant Volume.—From the specific heat at constant pressure it is now possible to compute the specific heat at constant volume by the well known formula for the difference of the two specific heats, namely $C_p - C_v = -\frac{\tau\left(\frac{\partial v}{\partial \tau}\right)_p^2}{\left(\frac{\partial v}{\partial p}\right)_\tau}$. This formula involves only quantities which have already been determined, so that C_v may be found immediately. The values of $\left(\frac{\partial v}{\partial \tau}\right)_p$ and $\left(\frac{\partial v}{\partial p}\right)_\tau$ used in this computation were taken from the tables, not from the diagrams. Just as for the specific heat at constant pressure, the values found in this way are the differences between C_v at atmospheric pressure and the pressure in question. The differences are such that a positive value means that the specific heat is greater at atmospheric pressure than at the pressure in question. A decreasing curve indicates, therefore, that the specific heat is increasing with increasing pressure.

In the paper on water other quantities of thermodynamic interest were plotted. These are the temperature effect of compression and the adiabatic compressibility. They may be easily calculated from the data given in this paper. While they are of interest in themselves, they do not seem to be of such fundamental importance as the quantities already listed in suggesting the possible internal mechanism of the liquid. It was felt, therefore, that to give them would unduly increase the volume of this paper, and they have accordingly not been computed.

A word seems called for as to the general character of the curves. In many cases there are slight irregularities which may very well not correspond to the actual facts, the irregularities being beyond the limit of experimental accuracy of the work. It is true that if each of these quantities were being given for itself alone, without con-

nection with other quantities, it would not have been justifiable to retain all the irregularities which some of the curves show. The reason for retaining the irregularities is that the attempt has been made to present a set of data which should be thermodynamically consistent. Let us suppose, for example, that the compressibility and the dilatation were both determined from the original tables of volumes and that they have been plotted against pressure. Both of these curves show irregularities which may be smoothed off by drawing smoother curves through the points, thus giving values of the compressibility and the dilatation which doubtless in themselves represent with greater probability the actual compressibility and dilatation. But each of these modified values for the compressibility and the dilatation will have a reflex effect on the table of volumes, which has now become inconsistent with the better values of the compressibility and the dilatation, and must therefore be altered slightly so as to be in accord with the new values. The alteration in the table necessary to accomplish this may be produced by changes less than the possible experimental error. But the point is this. Either the revised value of the compressibility or of the dilatation is sufficient of itself to completely revise the table of volume. If we are to adjust the compressibility or the dilatation we must do it so that both have the same reflex action on the table. Furthermore, all seven thermodynamic quantities must be adjusted in the same way. It is evident that this is a task of no small difficulty. To perform it, the only method seems to be a tedious one of trial and error. The labor of such an adjustment would be far beyond the labor of making the measurements with greater accuracy, and the labor had much better be so used in performing new experiments. It must furthermore be remembered that the values in the tables have been smoothed once with respect to both temperature and pressure. Any further changes would amount simply to slight changes in this smoothing; changes which were not justifiable by an examination of the data themselves but are rendered probable only by an examination of certain derived quantities. The choice has been made in this paper, therefore, to present results which may be slightly in error when taken by themselves, but which are nevertheless consistent thermodynamically.

IV. Numerical Details of Experiment and Computation.

In the detailed discussion and presentation of the results for the twelve liquids which is to follow, there will be given the experimental

accuracy to be expected for each liquid (because for some liquids the accuracy is greater than for others), and also the sources and the numerical values of the results of other observers which have been used in computing the results given here. The results taken from other work are the density at atmospheric pressure, the thermal dilatation, the initial compressibility for low pressure ranges, and the specific heats at atmospheric pressure. Unless otherwise specified, the values for the density at atmospheric pressure have been taken from the recent tables of Kaye and Laby, and the values for the thermal dilatation have been deduced from the tables of Landolt and Börnstein. In these tables the volume at any temperature is given in terms of the volume at 0° by a power series of the form $V_t = V_0 (1 + at + bt^2 + ct^3)$. In reproducing this expression it will not be necessary to repeat the formula each time, but merely to give the values of the three constants a, b, and c.

It has been mentioned on page 22 that in computing the changes of volume with pressure at 40°, it was found that beyond 500 kgm. the shape of the curves was nearly the same for all twelve liquids, the only difference being in the numerical magnitudes. The constants used in the general pressure-volume formula of page 22 for the average of the twelve liquids were as follows; $\alpha = -0.0029$, $\beta = -0.0546$, $\gamma = +0.2969$, and $\delta = -0.1804$. To pass from this general formula to any one of the twelve liquids each of these four constants is to be multiplied by the same factor. This factor will be given in the following under the name of the "reduction factor."

The discussion is to be one of merely the numerical details of the measurements and the computations. The discussion of the general character of the results and their significance will be reserved until the data have all been presented.

Methyl Alcohol.— Three sets of measurements were made on this substance with three different fillings of the apparatus, the last being separated by nearly three months from the earlier two. The first measurement was of the thermal dilatation and compressibility at low pressures with the larger bulb adapted for low pressure work. The next set of measurements, made immediately afterwards, was of the compressibility and dilatation at the higher pressures with the smaller bulb for the high pressure work. The third measurement was with the high pressure bulb, and included the compressibility and dilatation over the entire pressure range, both high and low pressures. The measurements at low pressures were made, as already explained, before the piston had been upset by the higher

pressures. The accuracy of the compressibility measurements may be estimated from the fact that the mean discrepancy of the piston displacements in the two sets of high pressure readings was 0.0035 inch, the maximum displacement being 2.07 inches. For the dilatation, the average discrepancy in the piston displacement for a rise of temperature of 20° was 0.0011 inch, the average displacement being 0.070 inch.

In computing the volumes at atmospheric pressure the density at 15° was taken to be 0.7960, from Kaye and Laby. The constants of the dilatation formula from Landolt and Börnstein are as follows; $a = 0.0_2 1186$, $b = 0.0_5 156$, $c = 0.0_8 91$[6]. This gives for the density at 0°, 0.8100. The quantity of methyl alcohol to which the tables and the diagrams refer weighs, therefore, 0.8100 gm. Since the boiling point of methyl alcohol is 64.7°, the volume listed in Table II for 80° and atmospheric pressure is, therefore, merely an extrapolation by means of the formula.

The "reduction factor" by means of which the transition was made from the mathematical formula for volume in terms of pressure at 40° to the experimental curve was 1.009.

The change of volume from 1 to 500 kgm. at 40° was taken as 0.0483, following Amagat. It should be noticed, however, that Amagat gives for the volume at 40° and atmospheric pressure 1.0438, against 1.0483 of the tables of Landolt and Börnstein. In this work the value 1.0483 was taken as the volume at 40°, but Amagat's value for the change of volume 1–500 kgm. was adopted without correction. At low pressures (20°) the present experimental values for the changes of volume were as follows: 1–500 atmos., 0.0530; 500–1000, 0.0294; 1000–1500, 0.0242; 1500–2000, 0.0199. The corresponding values of Amagat are 0.0480, 0.0300, 0.0239, 0.0194. The agreement is fairly good, except for the lowest pressure interval, where as has been pointed out, the present method can only indicate the probable result by an extrapolation. The newly published result of Richards is 0.0430 for the change of volume at 20° for an increase of 500 kgm. of pressure as against 0.0415 listed in the tables of volume.

The volume of methyl alcohol is shown as a function of pressure and temperature in Table II and in Figure 8.

The compressibility, β, of the first five alcohols has been measured by Pagliani and Palazzo,[7] who have collected their results into formulas of the type, $\beta_t = \beta_0 (1 + at + bt^2)$. Their pressure range was 1–4

6 Pierre, Ann. chim. et phys., **15**, 325 (1845).
7 Pagliani and Palazzo, Mem. R. Acc. Lin., **19**, 279 (1883/84).

atmospheres. Within this range the change of compressibility with pressure is negligible. The values found from their formulas (reduc-

TABLE II.

VOLUME OF METHYL ALCOHOL.

Pressure. kgm./cm.^{2}	Volume						
	20°.	30°.	40°.	50°.	60°.	70°.	80°.
1	1.0238	1.0361	1.0483	1.0610	1.0737	1.0869	1.1005
500	0.9823	0.9909	1.0000	1.0096	1.0197	1.0404	1.0416
1000	.9530	.9607	0.9684	0.9763	0.9844	0.9929	1.0023
1500	.9276	.9347	.9415	.9481	.9549	.9621	0.9697
2000	.9087	.9151	.9213	.9271	.9331	.9393	.9456
2500	.8930	.8988	.9044	.9098	.9151	.9205	.9260
3000	.8792	.8845	.8897	.8947	.8997	.9047	.9095
3500	.8663	.8712	.8761	.8808	.8854	.8899	.8944
4000	.8551	.8597	.8642	.8687	.8730	.8773	.8814
4500	.8449	.8492	.8535	.8577	.8618	.8657	.8695
5000	.8354	.8395	.8436	.8476	.8515	.8552	.8588
6000	.8192	.8232	.8271	.8307	.8344	.8379	.8412
7000	.8053	.8091	.8129	.8164	.8196	.8228	.8262
8000	.7936	.7972	.8008	.8040	.8070	.8108	.8134
9000	.7827	.7861	.7894	.7924	.7952	.7981	.8013
10000	.7725	.7757	.7788	.7818	.7847	.7876	.7905
11000	.7634	.7663	.7693	.7724	.7756	.7786	.7813
12000	.7559	.7586	.7614	.7647	.7682	.7712	.7738

tion being made from atmos. to kgm.) at 20°, 40°, 60°, and 80°, were 0.0_3113, 0.0_3124, 0.0_3142, and 0.0_3158 respectively. The values found from the present data by the method of computation outlined

on page 29 are 0.0_3101, 0.0_3124, 0.0_3137, and 0.0_3147 respectively. The means adopted for this paper are 108, 124, 140, and 152 respectively. There are also values for the compressibility by other observers, but not under conditions so nearly comparable with those here. These values are: 0.0_3104 at 14.7° and 0.0_3221 at 100° between 8.7

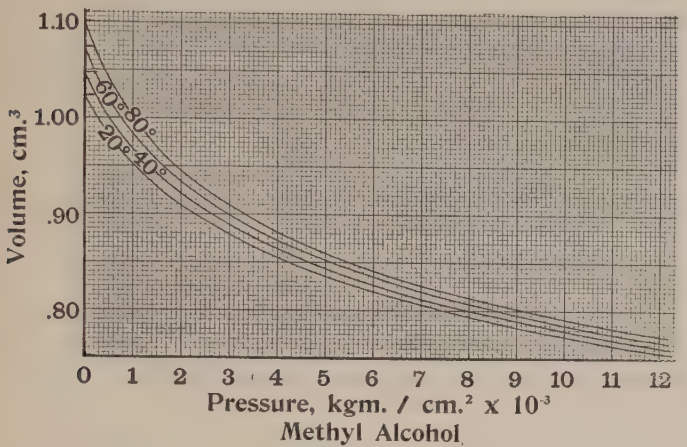

FIGURE 8. Methyl Alcohol. Volume at 20°, 40°, 60°, and 80° plotted against pressure. The lower curve gives the volume at 20°.

and 37 atmos. by Amagat[8]; 0.0_491 at 13.5° and 7.5 atmos. by Grassi[9]; 0.0_3108 at 2.7° and 8 atmos. and 0.0_3120 at 18° and 8 atmos. by Röntgen.[10] The newly published value of Richards for the compressibility at 20° is 0.0_3109 against 0.0_3108 adopted above.

There are a few measurements for the specific heat, C_p, at atmospheric pressure; 20.39 between 5° and 10°, 20.28 between 10° and 15°, and 20.76 between 15°and 20° by Regnault[11]; 22.29 between 23° and 43° by Kopp;[12] 21.56 between 5° and 13° by Lecher;[13] and 21.40 between 15.5° and 34.9°, 21.82 between 19.6° and 45°, 22.13 between 18.1° and 50.4°, and 22.77 between 20.5° and 63.2° by von Reis.[14]

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8 Amagat, Ann. chim. et phys., **11**, 520–549 (1877).
9 Grassi, Am. chim. et phys., **31**, 437 (1851).
10 Röntgen, Wied. Ann., **44**, 1 (1891).
11 Regnault, Ann. chim. et phys., **9**, 322 (1843).
12 Kopp, Pogg. Ann., **75**, 98 (1848).
13 Lecher, Wien Ber., **76**, 937 (1877).
14 von Reis, Wied. Ann., **13**, 447–465 (1881).

These values are in the units of this paper. It will be seen that the results of different observers do not agree within 5%. The results of von Reis, however, do justify us in assuming that C_p increases with rising temperature.

Ethyl Alcohol. More measurements were made on this than on most of the other substances, because it was the liquid with which the preliminary tests of the apparatus were made, but several of the early runs were not carried to completion because of accident. Measurements were made with five fillings of the apparatus. The first of the five fillings was made with the alcohol enclosed in a glass bulb, instead of in a steel one, as in the final experiments. This filling gave all the information desired at the low pressures, and also the thermal dilatation over nearly the entire high pressure range, but was terminated by polarization effects in the manganin. The polarization was found to be due to the breaking of the glass bulb, allowing the alcohol to diffuse to the coil. The readings before the break appeared should be trustworthy. The second of the five sets of measurements was of the compressibility at high pressures, and was completed without accident, but had to be discarded, for reasons that will appear later. The third set was of the dilatation and compressibility at high pressures. This also showed polarization, but not until the very end of the compressibility run. For the second and third runs a steel bulb was used, but the top was put on with soft solder. This soft solder gave way under pressure, allowing the kerosene to mix with the alcohol. The polarization probably did not occur as soon as the solder cracked, because it takes time for the alcohol to diffuse through the kerosene to the coil. The compressibility measurements of the third run are, therefore, more likely to be in error than the dilatation measurements, which were made a considerable time before the polarization appeared. Because the apparatus was the same, the second run is likely to be in error just as the compressibility measurements of the third, the polarization not having time to appear in the second run before the apparatus was taken apart. The early dilatation measurements were retained, therefore, and the early compressibility measurements discarded. The agreement of the early compressibility measurements, which presumably were made on a mixture of kerosene and ethyl alcohol, was good, 0.3%, but they were about 4% higher than the results of the final successful run. The last two of the five runs were carried through without accident, one being of the compressibility and dilatation at low pressures, and the other the corresponding measure-

ments for high pressures. For these, and for all subsequent runs, the top of the bulb was put on with silver solder.

TABLE III.

VOLUME OF ETHYL ALCOHOL.

Pressure. kgm./cm.²	Volume.						
	20°.	30°.	40°.	50°.	60°.	70°.	80°.
1	1.0212	1.0323	1.0438	1.0557	1.0679	1.0805	1.0934
500	0.9794	0.9873	0.9956	1.0044	1.0135	1.0233	1.0334
1000	.9506	.9570	.9636	0.9707	0.9781	0.9861	0.9944
1500	.9267	.9323	.9380	.9440	.9505	.9572	.9640
2000	.9081	.9131	.9182	.9235	.9291	.9349	.9407
2500	.8923	.8969	.9016	.9064	.9114	.9165	.9216
3000	.8786	.8830	.8874	.8919	.8964	.9010	.9055
3500	.8661	.8702	.8746	.8789	.8831	.8873	.8915
4000	.8545	.8586	.8628	.8668	.8708	.8747	.8787
4500	.8439	.8481	.8521	.8559	.8597	.8634	.8671
5000	.8343	.8383	.8424	.8461	.8498	.8533	.8568
6000	.8178	.8218	.8256	.8291	.8324	.8356	.8387
7000	.8038	.8075	.8110	.8142	.8171	.8200	.8229
8000	.7917	.7952	.7984	.8013	.8038	.8065	.8094
9000	.7807	.7840	.7868	.7893	.7917	.7954	.7973
10000	.7703	.7733	.7760	.7785	.7809	.7835	.7863
11000	.7606	.7633	.7659	.7693	.7713	.7741	.7765
12000	.7521	.7545	.7571	.7600	.7631	.7652	.7682

The average discrepancy of the piston displacement for a rise of temperature of 20° at constant pressure was 0.0016 inch, the mean displacement being about 0.070 inch.

The reduction factor from the mathematical formula for volume in terms of pressure at 40° was 0.9979.

The density at atmospheric pressure and 0° was taken as 0.8063. The constants of the dilatation formula of Landolt and Börnstein were $a = 0.0_21022$, $b = 0.0_5182$, $c = 0$. The values of the volume given

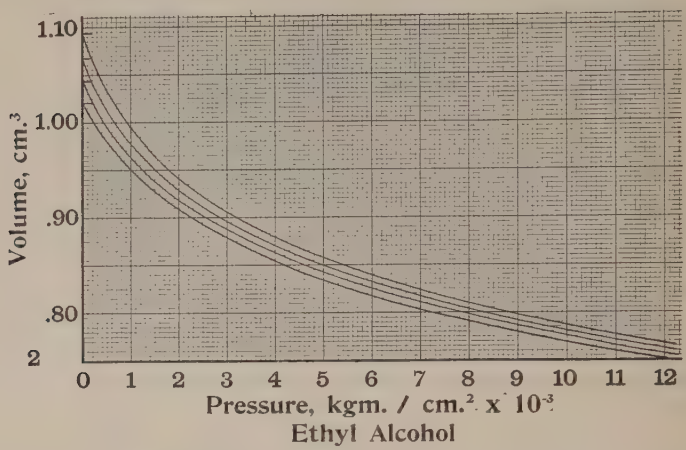

FIGURE 9. Ethyl Alcohol. Volume at 20°, 40°, 60°, and 80° plotted against pressure. The lower curve gives the volume at 20°.

by this formula are 1.0212, 1.0138, and 1.0679 at 20°, 40° and 60° respectively. We also have values of Pierre[15], which are 1.0216, 1.0448, and 1.0695 at the same temperatures respectively.

Amagat gives .0484 for the change of volume from 1 to 500 kgm. His value for the volume at 40° is 1.0442 against 1.0438 above. In the tables, 0.0484 was used as the change of volume 1–500, and 1.0438 as the volume at atmospheric pressure. At 20°, the change of volume between 1 and 500 atmos. was found to be 0.0477 against 0.0438 of Amagat. The numbers for the succeeding 500 atmos. intervals were 0.0287, 0.0236, 0.0193 against 0.0297, 0.0228, and 0.0188 of Amagat.

The volume as a function of pressure and temperature is given in Table III and in Figure 9.

The initial compressibilities at 20°, 40°, 60°, and 80°, computed as described, were found to be 0.0_3105, 0.0_3121, 0.0_3138, and 0.0_3151, respectively. The corresponding values of Pagliani and Palazzo are: 0.0_3102, 0.0_3114, 0.0_3130, and 0.0_3151. The agreement is as good as

[15] Pierre, Am. chim. et phys., **19**, 199 (1847).

could be expected for measurements for this nature. The means shown in the curves are: 0.0_3104, 0.0_3118, 0.0_3135, and 0.0_3151. Comparison may also be made with the values of Amagat,[16] which are

TABLE IV.

C_p FOR ETHYL ALCOHOL.

Observer.	Temp.	C_p (kgm. cm.).
Regnault [17]	—20°	17.37
	0°	18.81
	40°	22.63
	80°	26.44
Sutherland [18]	80°	24.49
	120°	31.27
Zetterman [19]	20°	31.23
De Heen and Deruyts [20]	40°	20.53
von Reis	15°.7–35°.1	19.93
	20°.7–45°.7	20.78
	18°.4–56°.0	21.32
	19°.8–62°.9	21.79
	20°.5–73°.4	22.44

0.0_4981 at 14° and 0.0_3196 at 99.4° at a mean pressure of 22 atmos. The agreement at the lower temperature is good; the upper temperature is beyond the range.

For C_p at atmospheric pressure we have a number of values which are shown in Table IV. The results are in very bad agreement, as may be seen by plotting them. It is however, perfectly certain that on the whole C_p for ethyl alcohol increases with rising temperature.

16 Amagat, 1. c. (1877).
17 Regnault, Mém. Acad., **26**, 262 (1862).
18 Sutherland, Phil. Mag., **26**, 298 (1888).
19 Zetterman, Akad. Afh. Helsingfors (1880).
20 De Heen and Deruyts. Bull de Belg., **15**, 168 (1888).

Propyl Alcohol.— Readings were made on this liquid with two fillings of the apparatus. The first was of the compressibility and the

TABLE V.

VOLUME OF PROPYL ALCOHOL.

Pressure. kgm./cm.²	Volume.						
	20°.	30°.	40°.	50°.	60°.	70°.	80°.
1	1.0173	1.0274	1.0380	1.0493	1.0612	1.0737	1.0865
500	0.9780	0.9864	0.9948	1.0034	1.0121	1.0213	1.0320
1000	.9498	.9571	.9641	0.9710	0.9779	0.9853	0.9934
1500	.9297	.9357	.9415	.9473	.9533	.9594	.9657
2000	.9142	.9192	.9242	.9293	.9344	.9396	.9448
2500	.9011	.9055	.9100	.9145	.9190	.9235	.9282
3000	.8897	.8937	.8979	.9021	.9062	.9103	.9145
3500	.8794	.8833	.8872	.8911	.8949	.8987	.9025
4000	.8700	.8738	.8776	.8813	.8849	.8884	.8919
4500	.8612	.8650	.8688	.8723	.8758	.8791	.8823
5000	.8529	.8567	.8604	.8639	.8671	.8702	.8732
6000	.8390	.8426	.8462	.8494	.8524	.8555	.8579
7000	.8266	.8300	.8333	.8363	.8391	.8416	.8442
8000	.8163	.8193	.8223	.8250	.8277	.8302	.8328
9000	.8069	.8098	.8124	.8150	.8175	.8201	.8230
10000	.7984	.8011	.8037	.8060	.8085	.8112	.8142
11000	.7909	.7934	.7958	.7980	.8004	.8031	.8061
12000	.7840	.7864	.7885	.7905	.7928	.7955	.7982

dilatation at the higher pressures, and the second was the complete set, both compressibility and dilatation at both high and low pressures. During the last set of readings, however, the moveable plug

pinched off at a high pressure because of fatigue, so that there is only one reading for the dilatation at the two highest pressures. The agreement between the two sets at the lower pressures was good enough however, so that it did not seem necessary to set the apparatus up again merely to repeat these last two readings.

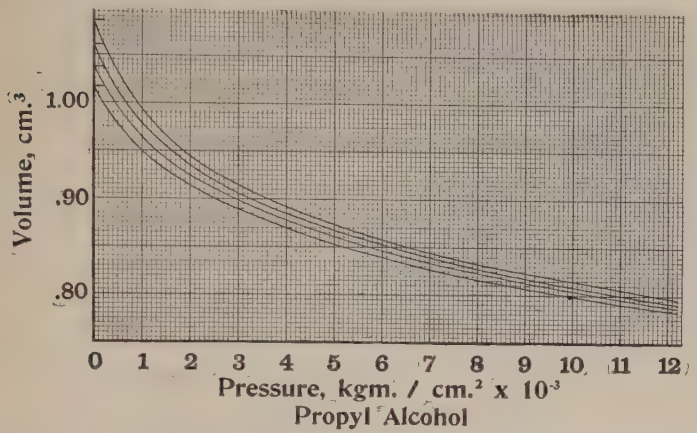

FIGURE 10. Propyl Alcohol. Volume at 20°, 40°, 60°, and 80° plotted against pressure. The lower curve gives the volume at 20°.

The average discrepancy between the piston displacement of the two determinations of the compressibility at high pressures was 0.0026 inch on a total stroke of 2 inches. The average discrepancy in the displacements at constant pressure corresponding to an increase of temperature of 20° was 0.0018 inch on a mean displacement of about 0.070 inch.

The reduction factor from the mathematical formula was 0.8726.

The density at 0° is 0.8179. The constants of the dilatation formula are: $a = 0.0_2774$, $b = 0.0_5497$, $c = -0.0_7141$. These values of a, b, and c are from results of Zahnder,[21] who gives for the density at 0° 0.8177, instead of 0.8179 above. The agreement is virtually perfect. In addition we have data by Naccari and Pagliani[22] who give for the density at 0° 0.8203, and for the volume at 20°, 40°, 60°, and 80°, 1.020, 1.042, 1.064, and 1.090 respectively, against 1.017, 1.038, 1.061, and 1.0865 adopted from Zahnder's formula above.

21 Zahnder, Lieb. Ann., **225**, 114–193 (1882).
22 Naccari and Pagliani. Att. R. Acc. dell. Sc., **16** (Sept. 1881).

Here again it seems as if the agreement between different observers should be better.

The volume of propyl alcohol as a function of pressure and temperature is given in Table V and in Figure 10.

At 40°, Amagat gives for the change of volume between 1 and 500 kgm. 0.0432, which is the value used in the table. He gives, however, 1.0406 for the volume at atmospheric pressure against 1.0380 adopted above. It will be noticed that Amagat's value lies between those of Zahnder and of Naccari and Pagliani. At low pressures and 20° the changes of volume for successive intervals of 500 atmos. were found to be: 0.0407, 0.0245, 0.0202, and 0.0170, against 0.0399, 0.0274, 0.0211, and 0.0176 of Amagat. The agreement for the lowest pressure interval is better than on the average. Richards in his recent paper gives a change of volume between 1 and 500 kgm. considerably smaller than that used here, namely 0.0355 against 0.0393. It should be remembered that the value used in this work for 20° is founded essentially on Amagat's value for 40°, the only difference being a small temperature correction determined from these present data. The disagreement just noted means therefore, that the values of Richards are considerably lower than those of Amagat.

The initial compressibilities at 20°, 40°, 60°, and 80° were as follows; to give the value of ΔV listed in the table 0.0_492, 0.0_3103, 0.0_3118, and 0.0_3130 respectively; the corresponding values of Pagliani and Palazzo are 0.0_490, 0.0_3101, 0.0_3115, and 0.0_3133. The agreement is good. The final values taken as a fair mean were: 0.0_491, 0.0_3102, 0.0_3117, 0.0_3131. Röntgen has also measured the compressibility at atmospheric pressure. His value for 20° would be 0.0_4955, judging from a linear extrapolation from his values at 4° and 18°. Richard's recent value at 20° is 0.0_4873, lower than any other of the values given above.

For C_p at atmospheric pressure we have the following values: — 21° to +12°, 18.02 by Nadejdine[23]; 21° to 23°, 22.99 by Pagliani;[24] 21° to 90°, 23.55 by Lougiunine[25]; and from 16.5° to 42.2°, 20.54, from 20.6° to 53.4°, 21.34, from 20.4°, to 65.2°, 21.99, from 19.5° to 78.5°, 22.63, and from 20.7° to 90.8°, 23.32 by von Reis. These results also indicate a considerable rise of C_p with rising temperature.

Isobutyl Alcohol.— Measurements on this were made with two fillings of the apparatus; the first gave the compressibility and the dilata-

23 Nadejdine, Jour. Russ. Phys. Chem. Ges., **16**, 222 (1884).
24 Pagliani, N. Cim., **11**, 229 (1882).
25 Lougiunine, Am. chim. phys., **13**, 289 (1898).

tion over the high pressure range, and the second the compressibility and dilatation over both the high and low pressure ranges. The use of isobutyl instead of normal butyl alcohol was not intended. In ordering the chemicals, normal butyl was not specified, and it was not noticed that the substance sent was isobutyl until all the preparations had been made for a run. This substance has the disadvantage, of not being one of the same series as the four other alcohols. However, it makes little difference so far as the comparison of the results with those of Amagat is concerned, for Amagat did not work with either normal- or iso-butyl alcohol. Furthermore, the use of this substance has proved very instructive in showing that a change in the structural formula changes the properties even at high pressures. It might be expected that high pressures would wipe out variations due to structural differences, but such has not proved to be the case, at least to 12000 kgm.

The average discrepancy in the piston displacements of the two determinations of compressibility was 0.0024 inch on a total displacement of 2.0 inches. The mean discrepancy of the displacement for the thermal dilatation for 20° was 0.0008 inch on a mean of about 0.070 inch. The agreement between the two sets of readings for the highest temperature range, 60°–80°, was virtually perfect.

The reduction factor for the mathematical formula was 0.9342.

Landolt and Börnstein's tables do not contain the requisite data for the volume of isobutyl alcohol at atmospheric pressure. The values adopted here were obtained by Naccari and Pagliani, and are apparently the only data which have been published for this liquid. These authors have not expressed their results by a power series, but prefer instead to give the density for a considerable number of temperatures. By interpolation from their results the volumes at 20°, 40°, 60°, and 80° were found to be: 1.0195, 1.0406, 1.0625, and 1.0880. From these results the value of Kaye and Laby for the density at 18° is reduced to 0.8165 at 0°, against 0.8162 of Naccari and Pagliani, virtual agreement.

No measurements of the change of volume of isobutyl alcohol had been made beyond a few kgm. previous to these computations, so the value obtained from the low pressure determinations of the present work was adopted. This was 0.0484 at 40° between 1 and 500 kgm.; not at all an unlikely value, being the same as Amagat's for ethyl alcohol. Compressibility determinations of others at low pressures have shown that isobutyl alcohol has a compressibility considerably higher than that of normal butyl alcohol, so that we are to expect a

value higher than we should predict from the behavior of propyl alcohol and a value as large as that of ethyl alcohol does not seem

TABLE VI.

VOLUME OF ISOBUTYL ALCOHOL.

Pressure. kgm./cm.²	Volume.						
	20°.	30°.	40°.	50°.	60°.	70°.	80°.
1	1.0195	1.0300	1.0406	1.0414	1.0625	1.0744	1.0880
500	0.9751	0.9838	0.9922	1.0006	1.0093	1.0184	1.0277
1000	.9486	.9560	.9632	0.9701	0.9768	0.9840	0.9918
1500	.9268	.9330	.9391	.9448	.9505	.9565	.9630
2000	.9097	.9150	.9202	.9252	.9303	.9355	.9410
2500	.8956	.9001	.9048	.9094	.9141	.9187	.9235
3000	.8822	.8867	.8905	.8949	.8994	.9038	.9080
3500	.8705	.8743	.8782	.8823	.8867	.8908	.8947
4000	.8601	.8637	.8673	.8712	.8755	.8794	.8830
4500	.8507	.8541	.8577	.8614	.8655	.8692	.8726
5000	.8409	.8443	.8477	.8513	.8552	.8587	.8619
6000	.8269	.8301	.8335	.8369	.8403	.8433	.8463
7000	.8130	.8163	.8196	.8228	.8260	.8289	.8317
8000	.8028	.8060	.8092	.8123	.8154	.8183	.8210
9000	.7927	.7959	.7990	.8021	.8050	.8079	.8105
10000	.7832	.7863	.7894	.7924	.7953	.7980	.8007
11000	.7742	.7772	.7803	.7833	.7862	.7888	.7913
12000	.7662	.7692	.7722	.7751	.7780	.7805	.7827

unlikely. The recent work of Richards gives for the change of volume at 20° between 1 and 500 kgm. 0.0355, against 0.0344 used in the tables. The agreement is as close as could be expected when the rough nature

of the present determinations at the low pressures is considered; the agreement is better than the agreement of those values which have been taken directly from the work of Amagat.

The volume of isobutyl alcohol as a function of pressure and temperature is shown in Table VI and in Figure 11.

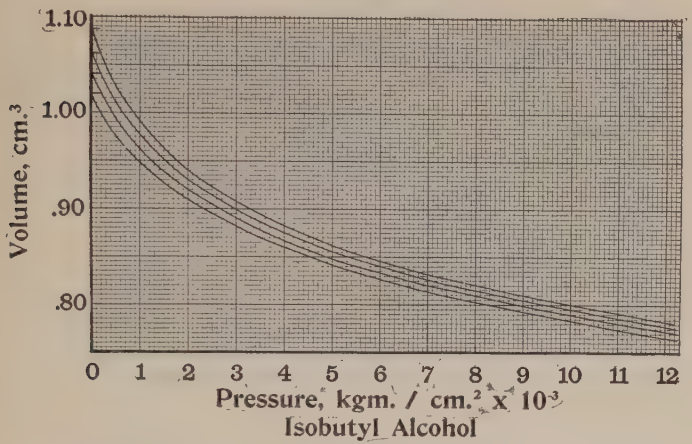

FIGURE 11. Isobutyl Alcohol. Volume at 20°, 40°, 60°, and 80° plotted against pressure. The lower curve gives the volume at 20°.

The compressibility determinations of Pagliani and Palazzo were fortunately made with isobutyl instead of normal butyl alcohol. They give for 20°, 40°, 60°, and 80° the values 0.0_492, 0.0_3103, 0.0_3118, and 0.0_3137. The values required to give the values of ΔV listed in the tables are 0.0_3122, 0.0_3133, 0.0_3144, and 0.0_3164. The discrepancy is large, too large. Instead, however, of taking the average of the discordant results, it was preferred to retain the values consistent with the table, it being understood that the initial values between 1 and 500 kgm., both for the total change of volume and for the compressibility are probably in error. Abnormal variations of compressibility, such as the rapid initial decrease with pressure, may possibly explain part of the discrepancy. We have also a value of Röntgen for the compressibility at 20°, 0.0_496, which is in very much better agreement with the value of Pagliani and Palazzo than the present value. The recent value of Richards is practically the same as Röntgen's.

For C_p we have a larger number of measurements than we should

expect from the small number of dilatation measurements. These values are shown in Table VII. When plotted, they show considerable discrepancies. The value at $-5°$ of Nadejdine and that of Pagliani are almost certainly in error. The other points lie roughly

TABLE VII.

C_p FOR ISOBUTYL ALCOHOL.

Observer.	Temperature.	C_p (kgm./cm.)
Longuinine [26]	20°–114°	24.00
	21°–109°	24.94
Nadejdine [27]	−21°–+10°	17.70
	16°–70°	21.39
	18°–98°	23.24
de Heen and Deruyts [28]	10°	17.49
	40°	22.57
	85°	29.29
Pagliani [29]	26°–30°	23.90

on a straight line, such that C_p increases from about 15 at 0° to about 23 at 50°. This is a very considerable increase.

Amyl Alcohol.—Experiments were made on this with three fillings of the apparatus; the first for compressibility and dilatation at low pressures with the large bulb, the second for compressibility and dilatation over the high pressure range, and the third for compressibility and dilatation over both ranges, high and low. The runs were all accomplished without accident of any sort.

The average discrepancy of the piston displacement for compressibility at 40° was 0.0019 inch on about 2 inches. The corresponding discrepancy for changes of temperature of 20° at constant pressure was 0.00206 inch on an mean of about 0.070 inch.

[26] Louguinine, l. c.
[27] Nadejdine, l. c.
[28] De Heen and Deruyts, l. c.
[29] Pagliani, l. c.

The reduction factor from the mathematical formula was 0.8925, showing that at high pressures amyl alcohol is one of the most incompressible of the twelve liquids.

TABLE VIII.

VOLUME OF AMYL ALCOHOL.

Pressure. kgm./cm.²	Volume.						
	20°.	30°.	40°.	50°.	60°.	70°.	80°.
1	1.0181	1.0270	1.0374	1.0476	1.0583	1.0694	1.0814
500	0.9800	0.9880	0.9959	1.0039	1.0122	1.0210	1.0304
1000	.9526	.9593	.9660	0.9724	0.9792	0.9863	0.9936
1500	.9325	.9383	.9440	.9495	.9551	.9608	.9667
2000	.9158	.9210	.9259	.9307	.9354	.9402	.9452
2500	.9015	.9064	.9107	.9149	.9190	.9232	.9277
3000	.8892	.8938	.8979	.9018	.9055	.9094	.9136
3500	.8780	.8823	.8864	.8900	.8935	.8971	.9010
4000	.8682	.8725	.8764	.8800	.8832	.8867	.8903
4500	.8593	.8635	.8673	.8708	.8739	.8772	.8807
5000	.8508	.8548	.8585	.8618	.8648	.8679	.8713
6000	.8373	.8409	.8442	.8471	.8501	.8530	.8560
7000	.8251	.8281	.8310	.8337	.8363	.8390	.8418
8000	.8149	.8176	.8201	.8225	.8250	.8274	.8302
9000	.8044	.8068	.8092	.8114	.8138	.8163	.8190
10000	.7948	.7971	.7994	.8018	.8041	.8066	.8091
11000	.7860	.7886	.7904	.7932	.7954	.7976	.8001
12000	.7782	.7803	.7826	.7854	.7882	.7905	.7926

The density at 0° and atmospheric pressure was taken as 0.8266. The constants of the dilatation formula were: $a = 0.0_289$, $b = 0.0_657$,

$c = 0.0_7118$. This formula of Landolt and Börnstein seems to be taken from Pierre.[30] It gives for the volumes at 20°, 40°, 60°, and 80° the values 1.0181, 1.0374, 1.0583, and 1.0814 respectively. We have also the following values by Pierre and Puchot[31]; 1.0187, 1.0397, 1.0610, and 1.0864. These authors give for the density at 0°, 0.817.

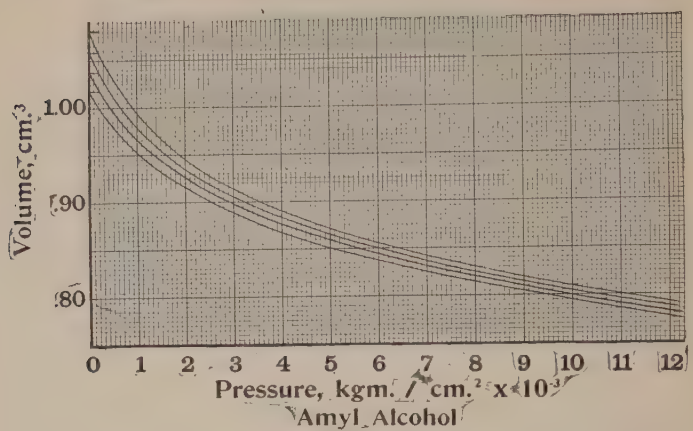

FIGURE 12. Amyl Alcohol. Volume at 20°, 40°, 60°, and 80° plotted against pressure. The lower curve gives the volume at 20°.

Zahnder[32] gives for the density at 0° 0.829, and for the constants of the dilatation formula, $a = 0.0_3919$, $b = -0.0_6461$, and $c = 0.0_7175$? Here again the discrepancies appear to be greater than they should in measurements of this character.

For the change of volume between 1 and 500 kgm. there seem to be no other data as a basis of comparison. Amagat used allyl instead of amyl alcohol for some unknown reason. The only course, therefore, was to accept the value given by this present work for the lower pressure interval, namely 0.0451. That this figure is about correct, however, is spoken for by the rather unusually close agreement of the two measurements of the piston displacement at 20°, 0.389 inch and 0.379 inch, a disagreement of 2.5%.

The volume of amyl alcohol as a function of pressure and temperature is shown in Table VIII and in Figure 12.

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30 Pierre, l. c. (1847).
31 Pierre and Puchot, Ann. chim. et phys. (4), **22**, 306?
32 Zahnder, l. c.

For C_p we have the following values: 19.89 by Kopp[33] for the temperature range 26°–44°; 24.43 by Regnault[34] for the range 10°–117°; 24.51 by Louguinine[35] between 21° and 130°; and 22.97 between 20.5° and 100.1°, 23.64 between 22.2° and 111.6°, and 24.23 between 22.2° and 124.5° by von Reis. These values, which are rather more consistent than usual, show a fairly rapid increase of C_p with temperature.

Ether.—Measurements were made on this liquid with four different fillings of the apparatus. The first two, made before the method had been perfected, were neither complete because of accidents, but between them they give completely the compressibility and the dilatation over the entire high pressure range. The third set of readings was over the low pressure range; this set was repeated without refilling the apparatus. The fourth set, made with the perfected apparatus, was over the high pressure range, and was completed successfully without accident.

There were three sets of piston displacements for the compressibility at 40°. The mean discrepancy of these was $\frac{1}{2}\%$ on the maximum displacement, which is below the average in accuracy. The mean discrepancy of the piston displacements for the thermal dilatation was 0.0022 inch on about 0.070 inch, which is nearly normal.

The reduction factor from the mathematical formula was 1.104, showing that over the entire range ether remains more compressible than any of the other liquids, except ethyl chloride.

The low boiling point of ether at atmospheric pressure, 34.6°, makes it impossible to tabulate the initial properties at the higher temperatures. For this reason many of the curves start at 500 kgm. as the zero instead of atmospheric pressure.

The density of ether at atmospheric pressure and 0° was 0.7382. The three constants of the dilatation formula had the values: $a = 0.0_2 1513$, $b = 0.0_5 236$, and $c = 0.0_7 400$.[36]

The change of volume at 40° between 1 and 500 kgm. was taken from Amagat as 0.0770. Amagat gives for the volume at 40° and atmospheric pressure 1.0672 against 1.0669 of the dilatation formula above. Amagat's value for the volume at 40° and 500 kgm. was corrected, therefore, in accordance with the above. The low pressure measurements of this present work at 20° are in unusually good agreement with Amagat; 0.0665 against 0.0656 for the interval 1–500

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33 Kopp, l. c.
34 Regnault, l. c. (1862).
35 Louguinine, l. c.
36 Pierre, l. c. (1845).

atmos.; 0.0370 against 0.0379 between 500 and 1000; 0.0272 against 0.0275 between 1000 and 1500; and 0.0216 against 0.0215 between

TABLE IX.

VOLUME OF ETHER.

Pressure. kgm./cm.²	Volume.						
	20°.	30°.	40°.	50°.	60°.	70°.	80°.
1	1.0315	1.0492	1.0669				
500	0.9681	0.9790	0.9899	1.0011	1.0124	1.0247	1.0387
1000	.9363	.9445	.9530	0.9616	0.9707	0.9804	0.9906
1500	.9093	.9153	.9221	.9291	.9364	.9438	.9516
2000	.8871	.8980	.8980	.9038	.9099	.9164	.9223
2500	.8685	.8734	.8785	.8837	.8890	.8943	.8997
3000	.8530	.8576	.8623	.8670	.8718	.8765	.8912
3500	.8395	.8440	.8483	.8526	.8570	.8613	.8654
4000	.8275	.8318	.8359	.8400	.8439	.8478	.8515
4500	.8168	.8209	.8249	.8287	.8324	.8359	.8393
5000	.8071	.8111	.8149	.8186	.8220	.8253	.8284
6000	.7916	.7954	.7989	.8023	.8055	.8085	.8112
7000	.7773	.7806	.7838	.7869	.7899	.7927	.7953
8000	.7645	.7675	.7704	.7732	.7759	.7786	.7813
9000	.7525	.7554	.7580	.7606	.7632	.7658	.7687
10000	.7418	.7444	.7469	.7496	.7520	.7547	.7574
11000	.7312	.7335	.7360	.7388	.7418	.7445	.7469
12000	.7216	.7237	.7261	.7289	.7316	.7342	.7365

1500 and 2000. It may be expected, therefore, that the low pressure values of the various thermodynamic properties are rather more than usually accurate for ether.

The volume of ether as a function of pressure and temperature is shown in Table IX and in Figure 13.

For the initial compressibility at 20° and 40° we have values of Amagat[37]; 0.0_3184, and 0.0_3218 respectively. There are also measurements by Avenarius[38] at 20° and 40°; 0.0_3191, and 0.0_3232, respec-

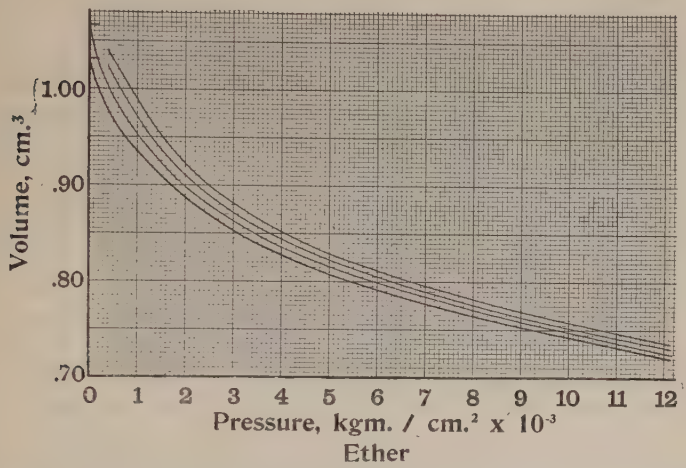

FIGURE 13. Ether. Volume at 20°, 40°, 60°, and 80° plotted against pressure. The lower curve gives volume at 20°. The curves for the higher temperatures could not be extended to the origin because of the low boiling point.

tively. The values needed to give the changes of volume listed in the table are 0.0_3170, and 0.0_3215. The mean values finally adopted were 0.0_3184, and 0.0_3220. There are also other measurements by Grimaldi[39] and Amagat at temperatures considerably above the normal boiling point, and at accordingly increased pressures, 20 kgm. or so. It was not attempted to make connections with these values.

C_p has been measured by Regnault[40], who gives 20.97 at 0°, and 21.69 at 30°; by Sutherland[41], whose values are 27.35 at 80°, and 31.86 at 120°; and by de Heen[42], who found 32.59 at 140°, and 41.27 at

37 Amagat, l. c., (1877).
38 Avenarius, Bull. Acc. St. Pet., **10** (1877).
39 Grimaldi, N. Cim., **19**, 7 (1886).
40 Regnault, l. c. (1862).
41 Sutherland, l. c.
42 de Heen, Bull de Belg., **15**, 522 (1888).

180°. These values all lie roughly on a curve passing through 20.0 at 0°, 23.5 at 40°, 27.0 at 80°, 31.0 at 120°, and 36.5 at 160°. The increase of C_p with temperature is fairly rapid, and becomes more rapid at the higher temperatures.

Acetone.— Two fillings of the apparatus with this substance were made. The high pressure measurements only were made with the first filling, and both high and low pressure readings with the second. Acetone was unique among the liquids used in that it froze under pressure. This was not anticipated nor desired, since, for one thing, it made impossible measurements at the lower temperatures and higher pressures. Furthermore, the separation of the solid phase is apparently accompanied or foreshadowed by complications in the behavior of the liquid, which it was not desired to encounter at the present stage. As a consequence of the freezing, the readings at 20° run only to 8000 kgm. The curves showing the average properties of acetone over the entire temperature range all show a break, therefore, at 8000 kgm. Below 8000 kgm. the average is over the range from 20° to 80°, but above 8000 the range is from 40° to 80°.

No attempt was made to follow out the freezing curve, or to determine accurately the equilibrium pressure at any temperature. It was found, however, that at 40° the freezing pressure is about 10000 kgm. The freezing point of acetone at atmospheric pressure is given by Kaye and Laby at − 95°. This raising of the freezing point by 135° seems to be larger than any previously recorded.

Acetone also showed one other peculiarity. When the liquid was examined at the close of the second run, it was found to be of a slight rose color, and there was a small amount of a fine white precipitate. The rose color deepened in the course of several days to a dirty brown, and the precipitate appeared to increase slightly in quantity. It was thought at the time that this was a chemical reaction brought about by pressure alone, but subsequent investigation showed that the effect was doubtless due to the presence of a slight impurity of phosphorus trichloride, left from the previous run. Phosphorus trichloride when mixed with acetone and allowed to stand at atmospheric pressure was found to produce very slowly the same discoloration and precipitate as observed after exposure to pressure. The effect of pressure apparently is merely to hasten the reaction. In a subsequent experiment, in which every trace of phosphorus trichloride had been carefully removed by prolonged heating, acetone was submitted to the pressures and temperatures of the regular experiment for a day, with absolutely no trace of discoloration. Unfortunately, no examination

was made of the condition of the liquid after the end of the first run, so it cannot be told whether the effect was present then or not; probably not. In any event the error so introduced is probably very small, because not more than a very small impurity of PCl_3 could have escaped attention in the weighing. There is, however, a slight possibility that the reaction was catalytic, in which event the error might be greater. The close agreement of the two sets of readings makes this unlikely, however.

The mean discrepancy in the piston readings for compressibility was about 0.005 inch on a total stroke of 2.0 inches. The first compressibility readings were made at 40° The liquid does not freeze until it has been considerably subcooled, so that it was possible to cover the entire pressure range at 40°. But in order to avoid the possibility of the liquid freezing the second time at a less degree of subcooling than at first, the second run was made at 60°, and then reduced to 40° for comparison with the first run. The average discrepancy of the displacements for thermal dilatation was 0.0013 inch on an average of 0.070 inch.

The reduction factor from the mathematical formula was 1.049, showing that acetone is more compressible than the average.

The boiling point of acetone is 56.5°, so that for this reason the initial point of the 80° curve is taken as 1000 kgm. The initial values at 60° were obtained by extrapolation, disregarding the boiling, and strictly apply only to a zero of a few kgm.

The density of acetone at atmospheric pressure and 0° was assumed to be 0.8136. The constants of the dilatation formula were: $a = 0.0_21324$, $b = 0.0_53380$, and $c = -0.0_88$. These constants are taken from data of Zahnder, who gives for the density at 0° 0.8125, and for the boiling point 56.3°, values slightly different from those given above.

The change of volume at 40° between 1 and 500 kgm. was taken as 0.0541 from Amagat. His value for the volume at 40° and 1 kgm., however, is 1.0575 against 1.0585 given by the formula above. The probable accuracy of the low pressure measurements of acetone may be judged from a comparison of the values at 20° with those of Amagat. For the successive pressure intervals 1–500, 500–1000, 1000–1500, and 1500–2000 atmos. the present work gave the following changes of volume; 0.0526, 0.0308, 0.0251, 0.0208, while Amagat gives 0.0483, 0.0325, 0.0245, and 0.0196.

The volume of acetone as a function of temperature and pressure is shown in Table X and in Figure 14.

The initial compressibility at 20°, 40°, and 60° may be computed from values of Amagat[43] at 14° and 99°, between 15 and 22 atmos.

TABLE X.

VOLUME OF ACETONE.

Pressure. kgm./cm.²	Volume.						
	20°.	30°.	40°.	50°.	60°.	70°.	80°.
1	1.0279	1.0426	1.0585	1.0752	1.0929		
500	0.9829	0.9931	1.0044	1.0165	1.0297		
1000	.9553	.9638	0.9728	0.9821	0.9924	1.0015	1.0107
1500	.9307	.9385	.9463	.9541	.9619	0.9694	0.9764
2000	.9100	.9173	.9243	.9309	.9374	.9436	.9497
2500	.8927	.8997	.9058	.9116	.9173	.9229	.9285
3000	.8775	.8841	.8897	.8948	.8999	.9051	.9105
3500	.8646	.8707	.8759	.8806	.8853	.8902	.8953
4000	.8532	.8586	.8636	.8681	.8725	.8771	.8819
4500	.8430	.8482	.8528	.8572	.8614	.8657	.8699
5000	.8334	.8380	.8425	.8469	.8510	.8549	.8586
6000	.8175	.8216	.8257	.8299	.8339	.8374	.8403
7000	.8028	.8064	.8103	.8145	.8182	.8215	.8243
8000	.7898	.7933	.7969	.8005	.8039	.8071	.8101
9000			.7847	.7879	.7910	.7942	.7974
10000			.7737	.7767	.7797	.7827	.7857
11000			.7634	.7667	.7697	.7725	.7750
12000			.7546	.7583	.7614	.7638	.7657

by a linear interpolation for temperature and by assuming the variation of compressibility with pressure found here. We obtain in this

[43] Amagat, l. c. (1877).

way from Amagat's data the following values: 0.0_3121, 0.0_3143, and 0.0_3194, respectively. The corresponding values from the present work to give the correct changes of volume are 0.0_3120, 0.0_3146, and 0.0_3167; rather good agreement except at 60°, where for one thing the linear interpolation from Amagat's data would be accountable for

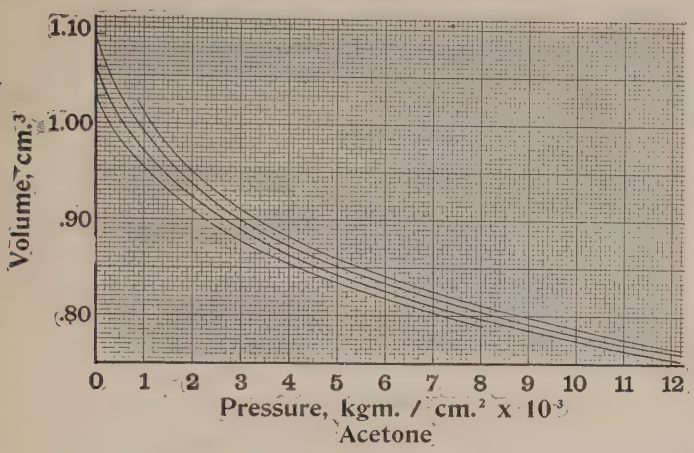

FIGURE 14. Acetone. Volume at 20°, 40°, 60°, and 80°, against pressure. The lower curve is for 20°. The curve for 20° is terminated at 8000 kgm. because acetone freezes at this point. The curve for 80° starts from 1000 kgm. because acetone boils at atmospheric pressure below 80°.

some of the divergence in the direction shown. The values taken as the average were; 0.0_3120, 0.0_3145, and 0.0_3167.

The only values we have for C_p are by von Reis, who gives 19.43 between 16.4° and 52.6°, 19.65 between 17.6° and 60.3°, 19.68 between 18.9° and 70.2°, and 19.72 between 18.7° and 79.1°. These data show an unusually slight increase of C_p with the temperature.

Carbon Bisulphide.— Three sets of measurements were made on this substance, the first of compressibility and dilatation at low pressures with the larger low pressure bulb, the second of compressibility and dilatation over the high pressure range with the smaller high pressure bulb, and the third of compressibility and dilatation with the smaller bulb over the entire pressure range. All of these runs were made without accident of any sort.

The average discrepancy of the two sets of piston displacements for the isothermal compressibility at 40° was 0.002 inch, on a total stroke of about 2.0 inches. The corresponding discrepancy for the

thermal expansion due to a change of temperature of 20° was 0.0013 inch for a mean displacement of about 0.070 inch. As far as self consistency goes, the measurements on carbon bisulphide are among the best of the series.

TABLE XI.

VOLUME OF CARBON BISULPHIDE.

Pressure. kgm./cm.²	Volume.						
	20°.	30°.	40°.	50°.	60°.	70°.	80°.
1	1.0235	1.0357	1.0490	1.0630	1.0775	1.0928	1.0992
500	0.9865	0.9964	1.0063	1.0158	1.0256	1.0359	1.0473
1000	.9586	.9671	0.9752	0.9829	0.9907	0.9991	1.0083
1500	.9358	.9432	.9504	.9571	.9639	.9709	0.9787
2000	.9173	.9240	.9302	.9362	.9423	.9485	.9552
2500	.9018	.9076	.9133	.9188	.9244	.9299	.9357
3000	.8877	.8928	.8981	.9033	.9084	.9134	.9185
3500	.8756	.8801	.8849	.8897	.8946	.8991	.9035
4000	.8647	.8688	.8732	.8770	.8823	.8855	.8902
4500	.8548	.8586	.8627	.8672	.8714	.8752	.8786
5000	.8453	.8489	.8528	.8570	.8610	.8645	.8676
6000	.8295	.8329	.8367	.8406	.8442	.8472	.8501
7000	.8147	.8184	.8222	.8257	.8290	.8319	.8347
8000	.8022	.8061	.8100	.8131	.8162	.8191	.8220
9000	.7911	.7954	.7989	.8020	.8049	.8078	.8107
10000	.7805	.7844	.7879	.7910	.7940	.7969	.7997
11000	.7715	.7745	.7777	.7809	.7839	.7867	.7894
12000	.7638	.7658	.7682	.7710	.7743	.7772	.7795

The reduction factor from the mathematical formula was 0.9947, showing pretty nearly average compressibility.

The density at 0° and atmospheric pressure was assumed to be 1.292. The three constants of the dilatation formula were as follows: $a = 0.0_2 1140$, $b = 0.0_5 137$, and $c = 0.0_7 191$.[44]

Amagat did not measure the volume of CS_2 at 40° at less than 600 atmos. The change of volume between 1 and 500 kgm. was found,

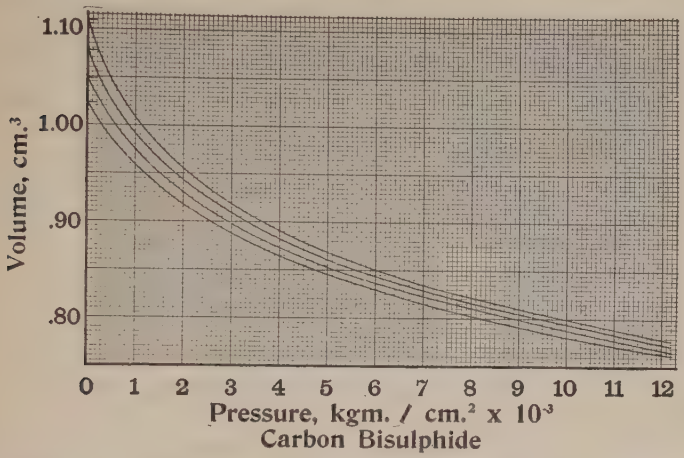

FIGURE 15. Carbon Bisulphide. Volume at 20°, 40°, 60°, and 80° plotted against pressure. The lower curve is for 20°.

therefore, by subtracting the value found here for 500–1000 kgm. from Amagat's value for the change 1–1000 kgm., giving the result 0.0427 between 1 and 500 kgm. Amagat's value for the volume at 40° and 1 kgm. is 1.0484 against 1.0490 given by the formula above. The present low pressure determinations gave results consistently higher than those of Amagat: These values were as follows: 0.0476 (not accurate) for 1–500 atmos., 0.0295 between 500 and 1000, 0.0227 between 1000 and 1500, 0.0198 between 1500 and 2000. For the same pressure intervals Amagat has 0.0387, 0.0277, 0.0222, and 0.0183.

The volume of carbon bisulphide as a function of pressure and temperature is shown in Table XI and in Figure 15.

The initial compressibilities at 20°, 40°, 60°, and 80° may be found from Amagat to have the values $0.0_4 90$, $0.0_3 107$, $0.0_3 128$, and $0.0_3 149$ respectively. The corresponding values required to give the change of volume listed in the tables are $0.0_4 92$, $0.0_3 107$, $0.0_3 133$, and $0.0_3 150$; good agreement. Röntgen also gives $0.0_4 87$ at 20°. The values

44 Pierre, l. c. (1845).

shown in the curves are the values to give the correct change of volume, except at 20°, where 0.0491 was adopted.

There are a number of measurements of C_p for CS_2. Regnault[45] gives 12.68 at −30°, 12.95 at 0°, 13.23 at 30°; Hirn[46] gives 13.13 at 30°; Sutherland[47] 14.33 at 80°, and 15.22 at 120°; and Forch[48] 13.34 at 18°. These results are more consistent than usual, lying on a smooth curve within about 1%. C_p increases with rising temperature, the rate of increase also increasing.

Phosphorus Trichloride.— Two sets of measurements were made on this substance; the first of compressibility and dilatation over the high pressure range, the second over the entire pressure range. Both sets of measurements were made with the smaller high pressure bulb. There was no accident.

The average discrepancy in the piston displacements for the isothermal compressibility at 40° was 0.006 inch on a stroke of about 2.0 inches. The discrepancy in the displacement for the dilatation was 0.0011 inch on 0.070 inch, mean.

The reduction factor from the mathematical formula was 0.9335, showing that PCl_3 is somewhat less compressible than normal.

The density at 0° and 1 kgm. was taken as 1.612. The three constants of the dilatation formula were $a = 0.0_21139$, $b = 0.0_5167$, and $c = 0.0_840$.[49] There are also values for the volume of PCl_3 by Pierre, who gives for 20°, 40°, and 60°: 1.0231, 1.0477, and 1.0747. The corresponding values computed with the above values for the constants are 1.0234, 1.0485, and 1.0752, rather better agreement than we have come to expect.

The change of volume at atmospheric pressure between 1 and 500 kgm. was taken from Amagat as 0.0445. Amagat gives for the atmospheric volume at 40°, 1.0483, in substantial agreement with 1.0485, given by the formula. At 20° and low pressures, the values found for the change of volume for successive intervals of 500 atmos. were, 0.0451, 0.0263, 0.0219, and 0.0187, against the values of Amagat; 0.0396, 0.0282, 0.0224, and 0.0186.

The volume of phosphorus trichloride as a function of pressure and temperature is given in Table XII and in Figure 16.

There seem to be no other determinations of the initial compressibility at atmospheric pressure. Accordingly, the values given in the

45 Regnault, l. c. (1862).
46 Hirn, Am. d. chim., **10**, 32 (1867).
47 Sutherland, l. c.
48 Forch, Ann. d. Phys., **12**, 202 (1903).
49 Thorpe, Jour. Chem. oc., **63**, 273 (1893).

tables are the values computed in the manner described on page 29 to give the correct changes of volume.

TABLE XII.

VOLUME OF PHOSPHORUS TRICHLORIDE.

Pressure. kgm./cm.²	Volume.						
	20°.	30°.	40°.	50°.	60°.	70°.	80°.
1	1.0234	1.0358	1.0485	1.0616	1.0752	1.0893	1.1039
500	0.9862	0.9949	1.0040	1.0136	1.0238	1.0346	1.0459
1000	.9593	.9666	0.9739	0.9816	0.9896	0.9980	1.0065
1500	.9382	.9445	.9509	.9575	.9643	.9712	0.9783
2000	.9205	.9262	.9318	.9377	.9437	.9498	.9557
2500	.9057	.9107	.9159	.9212	.9268	.9322	.9375
3000	.8926	.8973	.9022	.9072	.9123	.9171	.9220
3500	.8809	.8853	.8899	.8946	.8994	.9038	.9082
4000	.8705	.8747	.8790	.8836	.8880	.8922	.8962
4500	.8611	.8652	.8693	.8736	.8779	.8819	.8851
5000	.8521	.8560	.8600	.8641	.8682	.8720	.8757
6000	.8375	.8411	.8448	.8486	.8524	.8561	.8596
7000	.8245	.8279	.8313	.8347	.8382	.8416	.8450
8000	.8133	.8165	.8196	.8228	.8260	.8292	.8323
9000	.8029	.8059	.8089	.8120	.8150	.8180	.8210
10000	.7929	.7959	.7989	.8020	.8050	.8080	.8109
11000	.7838	.7866	.7897	.7927	.7957	.7985	.8014
12000	.7761	.7789	.7818	.7847	.7875	.7902	.7928

For C_p there seems to be only one determination, due to Regnault,[50] who finds the mean value 13.67 between 10° and 15°.

50 Regnault, l. c. (1843).

Ethyl Chloride.— Two sets of measurements were made on this substance, separated by thirty-six days in time, both with the smaller bulb, and both complete for compressibility and dilatation over the entire pressure range. Both runs were entirely without accident of any kind. The very low boiling point of this substance, 12.5°, and

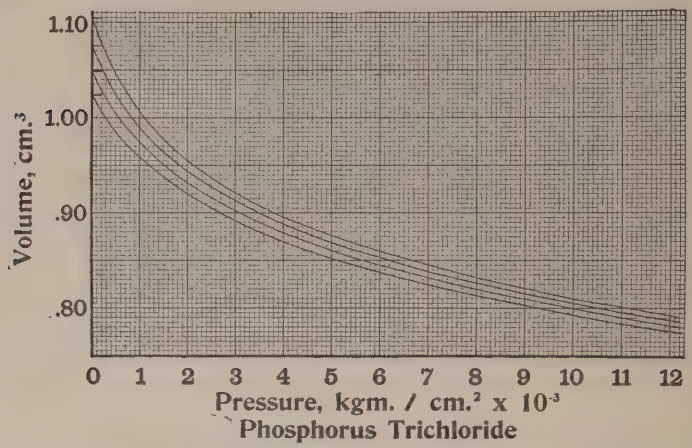

FIGURE 16. Phosphorus Trichloride. Volume at 20°, 40°, 60°, and 80° plotted against pressure. The lower curve is for 20°.

its abnormally high compressibility, made slight changes necessary in the details of the manipulation. The ethyl chloride was furnished by Kahlbaum, in sealed glass bulbs, which were accordingly exposed to an internal pressure greater than atmospheric. The steel compressibility bulb was filled after the ethyl chloride and the bulb had been brought to 0° in an ice bath. The steel bulb was then allowed to warm sufficiently to boil away a slight quantity of the ethyl chloride, when the capillary stem of the bulb was closed by forcing into it a small rubber stopper, considerably too large for it. The friction of the stopper was sufficient to hold it in place against the vapor pressure of the ethyl chloride at room temperature. The first application of a very moderate pressure by the pump was sufficient to drive the stopper into the bulb, where it remained during the rest of the measurements. In this way the filling could be accomplished without the troublesome necessity of cooling the large cylinder below 12° and maintaining it there until pressure could be applied. The small rubber stopper was

weighed, and its weight applied as a correction to the weight of the bulb full of the chloride. The weight was about 0.03 gm.

The piston displacement for isothermal compressibility at 40° showed a mean discrepancy of 0.0016 inch on a total of about 2.1 inches. The discrepancy in the displacements for dilatation averaged 0.002 inch on a mean of about 0.070 inch. The larger discrepancies were at the lower pressures; the mean above 2000 kgm. was 0.001 inch, half as much.

It has already been mentioned that ethyl chloride is so abnormally compressible that it was not possible to use the same formula as for the other eleven liquids to smooth the changes of volume at 40° for the tables. A formula of the same type was used, but with different coefficients (see page 22). The best values of the coefficients for ethyl chloride were found to be, $\alpha = 0.06723$, $\beta = 0.17139$, $\gamma = 0.04030$, and $\delta = -0.06261$. The maximum differences between the observed and the calculated change of volume were $+0.0007$ at 3000 kgm. and -0.0024 at 9000 kgm. The four constants were determined so that the curve passed through the experimental points at 500, 2000, 5000, and 12000 kgm. It should perhaps be mentioned that this formula is merely an empirical expression for the change of volume over the pressure range of the experiment. It has no theoretical significance whatever, and should not be used for purposes of extrapolation. For instance, it is seen immediately that it predicts an impossible behavior at infinite pressure.

The density at 0° was taken as 0.9120. The liquid boils at atmospheric pressure for every temperature within the range of the table. The ordinary dilatation formula would have been valueless, therefore, to fix the volume at any one point of the table. The fiducial point was taken at 40° and 500 kgm. from the data of Amagat,[51] who gives 0.9951 for the volume. The fact that the liquid boils at all temperatures of the table at atmospheric pressure has necessitated starting from 500 or 1000 kgm. as the initial point from which most of the thermodynamic properties have been computed.

The initial compressibilities given in the diagrams for 20° and 40° were taken from Amagat by interpolation and extrapolation from 22 atmos. The values are 0.0_3163, and 0.0_3211; they correspond to pressures somewhat higher than atmospheric.

The volume of ethyl chloride as a function of pressure and temperature is given in Table XIII and in Figure 17.

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51 Amagat, l. c. (1877).

For C_p we have apparently only one value, again due to Regnault,[52] who gives 16.80 at $-28.4°$, a temperature beyond the range of this work.

TABLE XIII.

Volume of Ethyl Chloride.

Pressure. kgm. cm.^{2}	Volume.						
	20°.	30°.	40°.	50°.	60°.	70°.	80°.
1							
500	0.9714	0.9831	0.9951	1.0075	1.0105	1.0339	1.0379
1000	.9276	0.9358	.9446	0.9544	0.9647	0.9741	0.9827
1500	.8988	.9059	.9132	.9211	.9296	.9373	.9444
2000	.8774	.8836	.8900	.8967	.9039	.9104	.9264
2500	.8596	.8652	.8709	.8768	.8831	.8888	.8938
3000	.8442	.8492	.8544	.8599	.8654	.8703	.8749
3500	.8311	.8358	.8405	.8456	.8506	.8551	.8591
4000	.8200	.8245	.8289	.8337	.8384	.8426	.8462
4500	.8087	.8129	.8172	.8217	.8262	.8301	.8335
5000	.7994	.8035	.8076	.8118	.8161	.8199	.8230
6000	.7821	.7860	.7900	.7938	.7976	.8010	.8040
7000	.7680	.7718	.7756	.7791	.7825	.7856	.7887
8000	.7561	.7597	.7633	.7666	.7699	.7730	.7762
9000	.7454	.7490	.7522	.7553	.7581	.7611	.7644
10000	.7352	.7385	.7415	.7444	.7473	.7502	.7533
11000	.7259	.7288	.7317	.7347	.7376	.7405	.7432
12000	.7176	.7199	.7225	.7254	.7286	.7314	.7336

Ethyl Bromide.— Two sets of measurements were made on this, both being with the smaller bulb and over the entire pressure range.

52 Regnault, l. c. (1862).

An interval of forty days separated the two sets. Both were completed without accident.

The average discrepancy of the piston displacements for isothermal compressibility at 40° was 0.0025 inch on a stroke of 2.05 inches. The mean discrepancy in the displacements for dilatation was 0.0013 inch on a mean of about 0.070 inch.

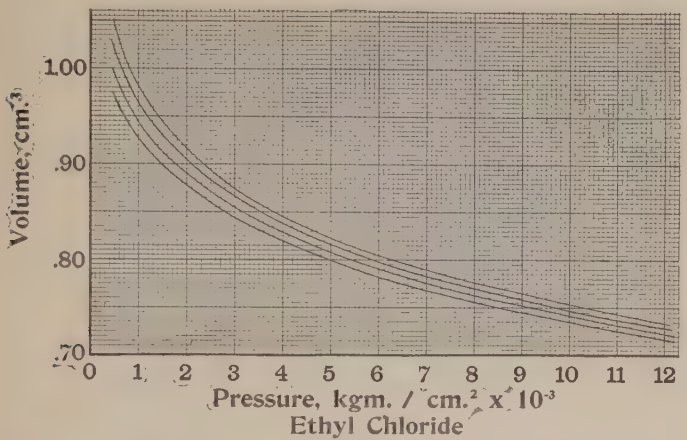

FIGURE 17. Ethyl Chloride. Volume at 20°, 40°, 60°, and 80° plotted against pressure. The lower curve is for 20°. The boiling point at atmospheric pressure is at 12°.5, so that it was necessary to take the origin of pressure as 500 kgm.

The reduction factor for passing from the mathematical formula was 1.032, indicating a compressibility somewhat more than normal.

The density at 0° and atmospheric pressure was assumed to be 1.483. The three constants of the dilatation formula were taken as $a_2 = 0.012275$, $b = 0.0_64437$, and $c = 0.0_70258$.[53] The boiling point of ethyl bromide is 38.4°. The formula gives for the volume at 20° 1.0249, and for the extrapolated value at 40°, 1.0515. Pierre also gives the volumes at 20° and 40°, 1.0275 and 1.0578 respectively. The discrepancies are large, 0.6% at 40°. In this case the preference has been given to the values of Pierre against those of Landolt and Börnstein, because Pierre actually measured the volumes at the temperatures in question, where as the formula of Landolt and Börnstein is directly applicable only at lower temperatures. Furthermore,

53 Pierre, l. c. (1845).

Amagat's value at 40°, 1.0583, agrees much more closely with Pierre's than with that given by the formula.

TABLE XIV.

VOLUME OF ETHYL BROMIDE.

Pressure. kgm. / cm.²	Volume.						
	20°.	30°.	40°.	50°.	60°.	70°.	80°.
1	1.0275	1.0418(?)	1.0578				
500	0.9788	0.9890(?)	1.0004				
1000	.9478	.9557	0.9644	0.9534	0.9824	0.9919	1.0018
1500	.9237	.9309	.9380	.9448	.9517	.9585	0.9654
2000	.9044	.9110	.9175	.9235	.9294	.9350	.9407
2500	.8885	.8950	.9011	.9066	.9120	.9170	.9218
3000	.8776	.8839	.8898	.8951	.9000	.9046	.9090
3500	.8610	.8670	.8725	.8775	.8821	.8864	.8904
4000	.8505	.8556	.8606	.8652	.8696	.8735	.8772
4500	.8410	.8455	.8500	.8543	.8585	.8622	.8657
5000	.8317	.8358	.8399	.8439	.8478	.8514	.8546
6000	.8163	.8201	.8237	.8273	.8307	.8340	.8371
7000	.8020	.8056	.8092	.8125	.8156	.8187	.8220
8000	.7900	.7935	.7968	.7999	.8028	.8059	.8091
9000	.7787	.7821	.7852	.7881	.7911	.7939	.7968
10000	.7686	.7717	.7747	.7777	.7807	.7834	.7858
11000	.7598	.7623	.7653	.7684	.7715	.7741	.7762
12000	.7521	.7546	.7572	.7601	.7633	.7659	.7677

The change of volume at 40° between 1 and 500 kgm. was taken as 0.0573 from Amagat. The values found here at 20° for successive intervals of 500 kgm., beginning at 1 kgm. were 0.0536, 0.0320, 0.0255,

and 0.0202, against 0.0492, 0.0322, 0.0248, and 0.0199 of Amagat. The agreement is rather good, except at the lowest pressure, where agreement is not to be expected. The just published value of Richards for the change of volume at 500 kgm. and 20° is 0.0446, against 0.0487 given in the table, which is essentially that of Amagat.

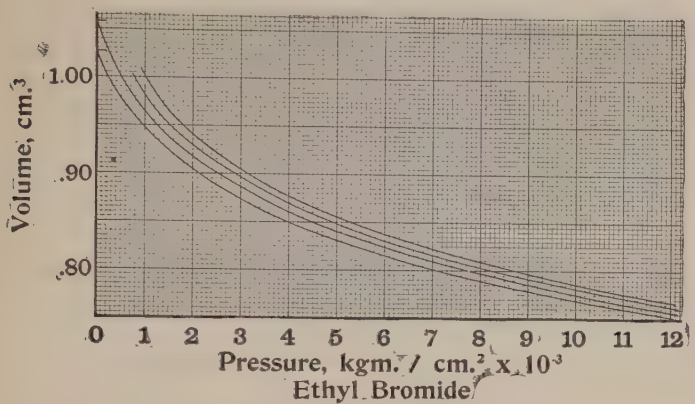

FIGURE 18. Ethyl Bromide. Volume at 20°, 40°, 60°, and 80° plotted against pressure. The lower curve is for 20°. The curves for 60° and 80° start from 1000 kgm. because the boiling point at atmospheric pressure is below 60°.

The volume of ethyl bromide as a function of pressure and temperature is given in Table XIV and in Figure 18.

When the computations of this paper were made the only value for the compressibility at low pressures was that of Amagat at 99° and a mean pressure of 20 atmos. This was too far removed from the range of this paper to justify any correction. The initial compressibilities at 20° and 40° were taken, therefore, so as to give the values of the changes of volume listed in the tables; $0.0_3 1248$ and $0.0_3 1476$ respectively. At 60° and 80° the compressibility is not given for pressures lower than 1000 kgm. The recently published data of Richards give for the compressibility at atmospheric pressure and 20° the value $0.0_3 106$, considerably lower than the value given above.

Regnault[54] gives a few values for C_p at atmospheric pressure; 14.62 between 5° and 10°, 14.42 between 10° and 15°, 14.54 between 15° and 20°. The temperature range is too small and the variations

54 Regnault, l. c. (1843).

too great to enable us to decide whether C_p really increases with temperature or not.

TABLE XV.

VOLUME OF ETHYL IODIDE.

Pressure. kgm./cm.²	Volume.						
	20°.	30°.	40°.	50°.	60°.	70°.	80°.
1	1.0214	1.0324	1.0438	1.0555	1.0677	1.0803	1.0935
500	0.9785	0.9880	0.9979	1.0081	1.0180	1.0276	1.0366
1000	.9502	.9584	.9665	0.9746	0.9825	0.9900	0.9969
1500	.9277	.9345	.9412	.9479	.9544	.9605	.9663
2000	.9092	.9150	.9209	.9266	.9323	.9375	.9425
2500	.8937	.8991	.9043	.9094	.9143	.9188	.9231
3000	.8802	.8851	.8899	.8945	.8988	.9028	.9065
3500	.8684	.8728	.8770	.8811	.8848	.8883	.8917
4000	.8583	.8621	.8659	.8694	.8728	.8759	.8790
4500	.8487	.8522	.8558	.8592	.8624	.8653	.8681
5000	.8394	.8429	.8463	.8496	.8529	.8557	.8581
6000	.8236	.8271	.8306	.8340	.8371	.8398	.8418
7000	.8093	.8129	.8164	.8193	.8220	.8243	.8264
8000	.7968	.8006	.8038	.8065	.8090	.8113	.8134
9000	.7856	.7902	.7922	.7945	.7967	.7989	.8013
10000	.7755	.7789	.7817	.7841	.7862	.7885	.7909
11000	.7665	.7694	.7722	.7747	.7771	.7794	.7817
12000	.7588	.7611	.7638	.7667	.7693	.7717	.7737

Ethyl Iodide.— Two runs were made on this with the smaller high pressure bulb over the entire pressure range, without accident. The mean variation of the displacement readings for compressi-

bility at 40° was 0.0020 inch on a total of 2.05 inches. The agreement is quite perceptibly better than the average. The thermal dilatation measurements show however, by far greater disagreement than any other of the twelve liquids. 0.0030 inch on a mean of 0.070 inch. The discrepancy was greater at the higher temperatures;

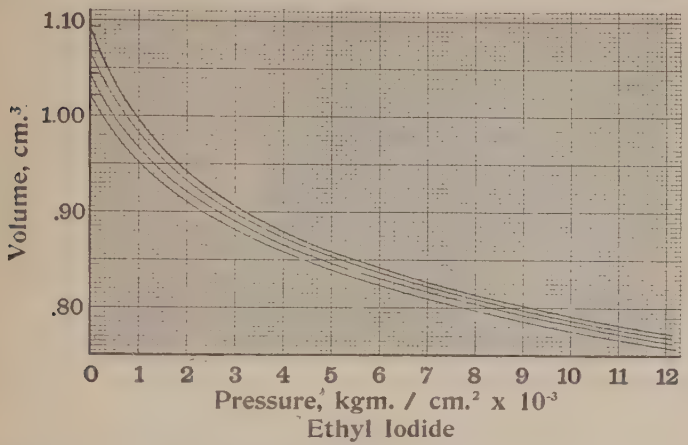

FIGURE 19. Ethyl Iodide. Volume at 20°, 40°, 60°, and 80° plotted against pressure. The lower curve is for 20°.

0.0012 inch from 20° to 40°, 0.0026 inch from 40° to 60°, and 0.0052 inch from 60° to 80°.

The reduction factor from the mathematical formula was 0.9817, showing slightly less than normal compressibility.

The density at 0° was assumed to be 1.973. The three constants of the dilatation formula were as follows: $a = 0.0_2 1054$, $b = 0.0_6 636$, and $c = 0.0_7 1004$.[55] Pierre also gives values for the volume at 20°, 40°, and 60° respectively; 1.0232, 1.0484, 1.0749, against 1.0214, 1.0438, and 1.0677 given by the formula. The agreement should be better. Probably Pierre's values are better, as is shown by the agreement of Amagat's value at 40°, but Pierre does not give the volume at 80°; so the value of the formula was accordingly selected.

The change of volume between 1 and 500 kgm. was taken from Amagat as 0.0459. Amagat gives for the initial volume at 40° 1.0486 against 1.0438 of the formula. The low pressure determina-

55 Dobriner, Lieb. Ann., **243**, 1–23 (1888).

tions of the change of volume at 20° gave for successive intervals of 500 atmos. 0.0509, 0.0278, 0.0233, and 0.0195 respectively, against 0.0404, 0.0289, 0.0227, and 0.0184 of Amagat. The agreement is fair, except of course for the first interval. The recent work of Richards gives 0.0370 for the change of volume at 20° and 500 kgm. against 0.0429 given in the tables. It is evident that the work of Richards and of Amagat is here in very essential disagreement.

The volume of ethyl iodide as a function of pressure and temperature is given in Table XV and in Figure 19.

When these computations were made there were no values of the initial compressibility with which to compare the results. Accordingly the value necessary to give the change of volume in the tables was used in every case. The recent data of Richards give 0.0_491 for the initial compressibility at 20°. This is considerably lower than the value shown in the curves, 0.0_4108. This simply means again that Richards finds a much smaller compressibility than Amagat.

C_p for ethyl iodide has apparently been determined only by Regnault[56]. He gives 13.19 at − 30°, 13.60 at 0°, 14.03 at 30°, and 14.44 at 60°. The increase with temperature is linear.

V. Discussion of Thermodynamic Properties.

In the following sections the general characteristics of the several thermodynamic functions will be discussed. The discussion will include suggestions as to what modifications it may possibly be necessary to make in our conceptions of a liquid, or what features that we have neglected at low pressures it may be necessary to emphasize at high pressures. Incidentally in the course of the discussion, suggestions will be made bearing on the theory of liquids, but any detailed examination of the problems that confront us in trying to frame a theory of liquids valid for high pressures will be reserved for section VI.

Volume.— The tables and diagrams of volume as a function of pressure and temperature have already been given, but with little comment.

One of the significant facts about the change of volume is in regard to the volume at infinite pressures, that is, the so-called volume of the molecules themselves, which is one of the quantities entering into nearly every theory of liquids. In particular, Tumlirz[57] and

56 Regnault, l. c. (1862).
57 Tumlirz, Sitz. k. Akd. Wiss. Wien, **118**, 1–39 (1909).

Tammann [58], in their recent theories, give values for the volume at infinite pressure. The values are listed in Table XVI for four of the liquids here investigated, and compared with the volumes found experimentally at 12000 kgm. and 20°. The observed value for ether at 12000 kgm. is actually less than the value predicted by either of

TABLE XVI.

Substance.	Volume.		
	Calculated, $p = \infty$		Observed. $p = 12000$.
	Tumlirz.	Tammann.	$t = 20°$
Methyl Alcohol	0.6970	0.7255	0.7559
Ethyl Alcohol	0.7037	0.7380	0.7521
Ether	0.7274	0.7246	0.7216
Carbon Bisulphide	0.6881	0.7246	0.7638

these theories for an infinite pressure; and for the other liquids the observed value is close to the predicted minimum. This result serves to emphasize more strikingly a point made in the preceding paper on water; namely, that at high pressures a liquid is more compressible than we might expect from its behavior at low pressures.

One line of inquiry is worth mentioning which seemed promising before the experiments were performed. The question, suggested by such properties of the atom as the atomic re-fraction, was this; is it possible at the higher pressures to assign to each atom its own specific volume as a function of the pressure, and so compute the volume of a compound at any pressure from its chemical constitution? But an examination of the changes of volumes of the two isomers, ether and isobutyl alcohol, shows that the supposed relation does not hold. For if we compare the volumes of equal weights, that is the volume occupied by the same number of atoms, we shall find that at atmospheric pressure the ratio of the volume of ether to that of isobutyl alcohol is 1.102, and that at 12000 kgm. it has dropped to 1.038. If the above relation were true, this ratio would be unity.

58 Tammann, l. c., see also Korber.

The fact that the ratio is approaching unity shows that the atoms are approaching the behavior suggested above, but if they ever reach it, it can only be at pressures considerably beyond those reached here.

In Table XVII are given the average volumes of the twelve liquids between 20° and 80°. This table corresponds to the diagrams for the average between 20° and 80° of the other thermodynamic properties; it will prove useful in plotting any of the average properties against volume, which may in some cases give more significant results than when pressure is used as the independent variable, as here.

Thermal Expansion. — The mechanism ordinarily assumed in explanation of thermal expansion is as follows. Any liquid is continually striving to expand, because of the thermal agitation of its molecules. The tendency to expand is resisted by two forces, the external pressure, and the forces of attraction between the molecules. An increase in temperature means an increase in the expanding force, which results in an increase of volume. This increase of volume would be expected to be greater if the force preventing expansion were less. Now the force preventing expansion becomes less as the volume becomes greater, because the cohesional forces decrease as the volume, or the distance apart of the molecules, becomes greater, The result is that the thermal dilatation increases with increasing temperature, that is with increasing volume. In other words, $\left(\frac{\partial^2 v}{\partial \tau^2}\right)_p$ is positive. Furthermore, as pressure increases, the force resisting expansion increases because of the decreased distance apart of the molecules, so that we are to expect a decreased dilatation at the higher pressures.

An examination of the curves for dilatation against pressure shows that these expectations are much more nearly fulfilled as regards the behavior of the dilatation with respect to pressure than with respect to temperature.

The general tendency of the dilatation of the separate liquids (Folder I, Figures 20 to 31) is to decrease with rising pressure. The decrease is very much more rapid at the lower than at the higher pressures. But beyond this general fact the curves give only an impression of bewildering complexity, crossing and recrossing in apparent disorder at the higher pressures. It is possible to find many instances where the dilatation increases with rising pressure over a range of several thousand kilograms, ultimately, however, to decrease again. One of the most striking examples of this is the 20° curve for carbon bisulphide; other well marked examples are afforded by ace-

TABLE XVII.

AVERAGE VOLUME BETWEEN 20° AND 80°.

Pressure. kgm. cm.²	Average Volume between 20° and 80°.											
	Methyl Alcohol.	Ethyl Alcohol.	Propyl Alcohol.	Isobutyl Alcohol.	Amyl Alcohol.	Ether.	Acetone.	Carbon Bisulphide.	Phosphorus Trichloride.	Ethyl Chloride.	Ethyl Bromide.	Ethyl Iodide.
1	1.0621	1.0573	1.0519	1.0538	1.0498	1.085†	1.075†	1.0664	1.0637		1.0755†	1.0575
500	1.0119	1.0064	1.0050	1.0014	1.0052	1.0034	1.0165	1.0169	1.0161	1.0097	1.0120†	1.0076
1000	0.9776	0.9725	0.9716	0.9712	0.9731	0.9635	0.9830	0.9835	0.9829	0.9552	0.9748	0.9736
1500	.9486	.9453	.9477	.9449	.9496	.9305	.9536	.9573	.9583	.9216	.9446	.9470
2000	.9271	.9244	.9295	.9254	.9305	.9047	.9299	.9363	.9381	.8969	.9226	.9259
2500	.9095	.9069	.9147	.9096	.9146	.8841	.9106	.9188	.9216	.8767	.9052	.9084
3000	.8943	.8920	.9021	.8951	.9014	.8671	.8943	.9031	.9073	.8596	.8933	.8934
3500	.8803	.8788	.8910	.8826	.8895	.8525	.8800	.8896	.8946	.8451	.8757	.8801
4000	.8682	.8666	.8810	.8716	.8793	.8395	.8676	.8775	.8834	.8331	.8639	.8687
4500	.8572	.8555	.8718	.8617	.8700	.8281	.8565	.8667	.8734	.8211	.8534	.8584
5000	.8471	.8455	.8631	.8514	.8611	.8178	.8460	.8565	.8639	.8112	.8432	.8488
6000	.8302	.8282	.8485	.8366	.8467	.8014	.8289	.8398	.8486	.7931	.8267	.8327
7000	.8157	.8134	.8354	.8224	.8335	.7863	.8136	.8247	.8348	.7784	.8120	.8179
8000	.8035	.8006	.8246	.8119	.8226	.7729	.8000	.8121	.8228	.7662	.7996	.8051
9000	.7920	.7890	.8150	.8016	.8117	.7606	.7911°	.8009	.8120	.7549	.7878	.7935
10000	.7815	.7783	.8063	.7920	.8020	.7496	.7797°	.7901	.8019	.7443	.7772	.7832
11000	.7723	.7695	.7985	.7828	.7931	.7391	.7692°	.7805	.7926	.7346	.7680	.7741
12000	.7668	.7602	.7911	.7745	.7854	.7291	.7602°	.7717	.7845	.7256	.7599	.7663

† Extrapolated to 50°.

° Average between 40° and 80°.

tone and ethyl-iodide. The rule, therefore, that dilatation decreases with rising pressure has many exceptions.

As regards the behavior of dilatation with respect to temperature, it is a striking fact that at the higher pressures the dilatation is usually greatest at the lower temperatures, instead of at the higher temperatures, as at atmospheric pressure. Every one of the diagrams shows this. What is more, the reversal of the effect in almost all cases takes place sharply at a definite pressure, the same for all temperatures; or in other words, the curves for the four temperatures, 20°, 40°, 60°, and 80° all cross at approximately the same point. This is exhibited still more strikingly in the curves for the average C_p of the twelve liquids (Figure 99). We have the thermodynamic formula $\left(\frac{\partial C_p}{\partial p}\right)_\tau = -\tau\left(\frac{\partial^2 v}{\partial \tau^2}\right)_p$, so that when the average value of $\left(\frac{\partial^2 v}{\partial \tau^2}\right)_p$ over the temperature range vanishes C_p will have a maximum. All of the curves show this maximum at the same pressure.

This universal reversal in the sign of $\left(\frac{\partial^2 v}{\partial \tau^2}\right)_p$ is a fact of no little interest and importance, and seems not to have been anticipated. In fact, the natural hypothesis of the contrary behavior, namely that at high pressures $\left(\frac{\partial^2 v}{\partial \tau^2}\right)_p = 0$, has recently been made the basis of an empirical theory of liquids by Tammann as was pointed out in the introduction. This hypothesis of Tammann is based on very plausible evidence from the data of Amagat, which seem to indicate that at high pressures $\left(\frac{\partial^2 v}{\partial \tau^2}\right)_p$ does vanish. But this apparent evidence from Amagat is founded on an accident, and a rather remarkable accident, as will be evident from an inspection of Figure 99 for C_p. The reversal in the sign of $\left(\frac{\partial^2 v}{\partial \tau^2}\right)_p$ takes place for nearly all the twelve liquids at pressures which are in the neighborhood of 3000 kgm., the maximum pressure reached by Amagat. As a matter of fact, Amagat's data do show in some cases the reversal of the effect, but the experimental error was fairly high, and Amagat himself did not credit the reversal as genuine. Only six of Amagat's liquids can yield evidence on this point, because they are the only ones for which readings were made at more then two temperatures; of these six liquids, ether, ethyl alcohol and carbon bisulphide show the reversal at 3000 kgm., while methyl and propyl alcohol and ethyl chloride show a positive $\left(\frac{\partial^2 v}{\partial \tau^2}\right)_p$ over the entire range.

At higher pressures there is in many cases, though not in all, a tendency for the effect to reverse again, that is, for the dilatation to again become greater at the higher temperature. The pressure of this second reversal is in the vicinity of 9000 or 10000 kgm. This fact also is indicated by the C_p curves.

A comparison of the curves for the different liquids shows a few features of interest. In the group of the five alcohols, isobutyl stands out as being the simplest, there being none of the crossing and recrossing which the others exhibit at the higher pressures. In this respect the four normal alcohols are much alike in their high pressure complications. That isobutyl alcohol should be different from the other alcohols was not anticipated before these experiments were made, since it seemed probable that at high pressure the effect of structural differences in the molecule would be eliminated. The effect of structural difference is also shown by a comparison of isobutyl alcohol and ether, since these two have the same formula, $C_4H_{10}O$. The high pressure effects are more complicated for ether. Acetone is peculiar in the wide divergence of the curves at the maximum pressure. It does not show any unusual effects in the neighborhood of the freezing point. It will be seen later that the specific heats are the quantities most susceptible to irregularities at the freezing point. Carbon bisulphide is remarkable for the curve at 20°, which shows a large increase of dilatation between 6000 and 9000 kgm., and also in this region shows a much greater dilatation than the curves for the higher temperatures. Phosphorus trichloride is the only one of the twelve liquids which behaves approximately as had been expected, since it shows little irregularity at the high pressures, and $\left(\frac{\partial^2 v}{\partial \tau^2}\right)_p$ nearly vanishes. The curves for the three ethyl halogen compounds do not show any particular progressive change of character such as one might expect, except with regard to the pressure at which $\left(\frac{\partial^2 v}{\partial \tau^2}\right)_p$ reverses in sign. This is shown best on the diagram for C_p. The pressure for reversal is lower than for most of the other liquids, and becomes less as the molecular weight of the compound increases. This may be because the increased molecular weight produces an increase in the cohesional force of attraction, and a consequent increase in the internal pressure, with the same effect as an increase of the external pressure. Ethyl iodide is remarkable for the low value of the dilatation at 80° at 6000 kgm. The minimum as 0.00017, and is lower than for any of the other liquids at the highest pressures.

It is evident that in order to explain these complicated facts we shall have to give up the simple picture of things that led us to expect the dilatation always to increase with increasing temperature and to decrease with increasing pressure. A natural way of modifying our conceptions so as to make room for these effects would seem to be as follows. We are to think of the molecules as having complicated shapes, or what for our purposes would amount to the same thing, of being surrounded by fields of force different in different directions. This concept does not seem to be a forced or an unlikely one; it must certainly be the fact for liquids which eventually crystallize under pressure, and for liquids which do not crystallize it is hard to conceive how an assemblage of atoms with unlike chemical affinities can coalesce into a molecule identical in all aspects. The effect of pressure on such an assemblage of molecules may be somewhat as follows. As the molecules are crowded closer together, the localized centers of force on the corners and edges play an increasingly individualized part, so that for small volumes we can no longer regard the molecules as centers of force and the cohesional force as a function of the mean distance apart of the molecules, but the orientation of the molecules with respect to each other begins to have its effect. Now we suppose that the natural tendency of the molecules in a liquid under normal conditions is to arrange themselves at haphazard with relation to each other. But as the constraints increase with decreasing volume, the characteristic shape compels an arrangement not entirely at haphazard, but such that the molecules fit into each other to some extent. Now it is evident that with the increasing orderliness of the arrangement of the molecules the relative positions of the localized centers of force will change. What is more, it is conceivable that the change in position of the force centers will be such that on the average the mean attraction between the molecules shall decrease with decreasing volume instead of increasing as is usual. Still more would this be true if there are centers of both attraction and repulsion in the molecule, as seems very likely from our present views of the electrical nature of matter. In this case we should expect the greater dilatation to be at the smaller volumes, because the cohesional force is less. But since the smaller volumes correspond to the lower temperatures, we have the effect already met, namely, that the dilatation is greater at the lower temperatures. The explanation of the sometimes increasing dilatation with rising pressure is similar. With increasing pressure the molecules may be forced to assume positions more regular in arrangement, of less volume, and of less average attractional

force also. The number of possible positions which the molecules may assume in this attempt to adapt themselves to the diminished space at their disposal may evidently be very great with molecules of at all complicated shapes, so that there is here the possibility of such very complicated dilatation curves as we actually have.

Another possible explanation which in the end amounts to very much the same thing for some purposes, is that of association. If we suppose that association takes place with decrease of volume, and that the amount of association is increased with increasing pressure, and is decreased with rising temperature, then we have also the possibility of decreasing dilatation with rising temperature and of increasing dilatation with rising pressure. In this case the phenomena are essentially similar to those of solidification under pressure of a mixture of different liquids. Such a case has already been investigated for kerosene, which shows the same general features as above. The phenomena for kerosene are much simpler than for these liquids, however. It is evident that one simple association (such as single to double molecules) is not sufficient of itself to explain the facts, but if we assume several associated molecules of varying degrees of complexity, and that the relative numbers of these change with pressure and temperature, the explanation would account for several of the facts actually found. But reasons will be given in the next section, for supposing that association cannot have a very large part in the phenomena at high pressures.

We now turn our attention to Figure 32, which gives in one diagram the average dilatation between 20° and 80° for all twelve liquids. The origin of each of these curves has been displaced downwards one unit with respect to the one above it. The origin is so located that the value of the thermal dilatation for each of the liquids at 12000 kgm. is between 0.0002 and 0.0003. The scale of the drawing is indicated at the side. The immediately striking feature is that the curves are nearly equi-spaced at the higher pressures. Approximate equal spacing of the curves would of course be a consequence of their all approaching zero, but this is not the entire effect by any means. For instance, the ratio of the dilatation of ether to that of amyl alcohol at low pressure is 1.50 while at 12000 kgm. pressure it has dropped to 1.03. (In the computation for ether, the initial dilatation at 20° was used.) This is only the first example of many we shall meet tending to show that at high pressures liquids lose the individual differences which characterized them at low pressures, and become more alike.

The very gradual change of dilatation with pressure at the high

pressures was also a surprise. The grand average for the dilatation at 12000 kgm. for the twelve liquids is 0.00025, about 40% more than that of mercury at atmospheric pressure and much higher than for any solid except possibly gutta-percha. It is ten times as great as that of aluminum, for example. The very slow change of dilatation

TABLE XVIII.

PRESSURE AT WHICH THE THERMAL EXPANSION IS TWICE AS LARGE AS IT IS AT 12000 KGM.

Substance.	Pressure. kgm./cm.²	Substance.	Pressure. kgm./cm.²
Methyl Alcohol	2150	Acetone	2900
Ethyl "	2000	Carbon Bisulphide	2900
Propyl "	2250	Phosphorus Trichloride	2200
Isobutyl "	1850	Ethyl Chloride	2750
Amyl "	2080	Ethyl Bromide	3100
Ether "	2750	Ethyl Iodide	2400

with pressure is shown in Table XVIII, giving the pressure at which the dilatation has twice its value at 12000 kgm. The table shows that between atmospheric pressure and 2400 kgm. (on the average) the dilatation falls to about 0.4 its initial value, while over a further pressure range four times as large it falls off only an additional 50%. From these data it would appear that the dilatation must remain very considerable for pressures far in excess of those reached here. The approximate equality of the pressures for the twelve liquids at which the dilatation is double its value at 12000 kgm. indicates that the liquids behave similarly over much the greater part of the pressure range.

The curves in general fall with increasing pressure, but all the alcohols show a tendency to become stationary or to rise; while carbon bisulphide shows an extended stationary region between 6000 and 10000 kgm. but beyond 10000 its curve drops with unusual steepness.

The four normal alcohols show a dilatation continually decreasing

with increasing molecular weight. But isobutyl alcohol shows the effect of its different structure by a higher dilatation than its position in the series would indicate. A comparison of isobutyl alcohol with ether, its isomer, shows that although initially the dilatation of ether is greater, at 12000 kgm. it has become less. This emphasizes again that the structure of the molecule continues to play a part even at high pressures. It is not to be wondered at in view of the suggested explanation of the complicated nature of the dilatation curves. For molecules of the same atomic formula, but of different structure, are to be thought of as possessing different shapes, and it is at high pressures that the effect of shape is greatest.

Isothermal Compressibility.— The isothermal compressibility is shown in Folder II; the values for the liquids separately at 20° intervals in Figures 33 to 44, and in Figure 45 the average results over the entire temperature range are collected into a single diagram for the twelve liquids.

The curves require a word of explanation. Up to 4000 kgm. the curves for each liquid are drawn for the four different temperatures, but at pressures higher than 4000 kgm. the curves would be so close together, sometimes crossing each other, that it would have been very confusing to draw them on the same scale. Therefore, at higher pressures, the only complete curve given is for 40°, while in the upper part of the diagram are shown on a larger scale the differences between the compressibilities for 20° intervals. The zero of these difference curves is drawn as a heavy line. Negative ordinates of the difference curve 20°–40° indicate that the compressibility is less at 20° than at 40°; positive values for the difference curve 40°–60° indicate a greater compressibility at 60° than at 40°, and similarly positive differences 60°–80° mean a greater compressibility at 80° than at 60°. To find the compressibility at 20°, one adds to the value obtained from the 40° curve the ordinates of the difference curve 20°–40° (this ordinate is usually negative); the compressibility at 60° is found by adding to the ordinate of the 40° curve that of the 40°–60° curve, and the compressibility at 80° by adding to that at 60° (obtained as above) the ordinate of the 60°–80° curve. A larger compressibility at 20° than at 40° is indicated by the difference curve 20°–40° rising from below and crossing the axis, while a smaller compressibility at 60° than at 40° is similarly shown by the curve 40°–60° crossing the axis from above. The mutual crossing of the difference curves, from this point of view, is not especially significant; it is the crossing of the axis that counts. The meaning of the mutual crossing of the curves 40°–60° and 60°–80°,

for example, would be that over the temperature range 40°–80°, $\frac{\partial^2}{\partial \tau^2}\left[\left(\frac{\partial v}{\partial p}\right)_\tau\right]_p = 0$.

The general behavior of the compressibility that one is prepared to expect from experiments at low pressures is a decrease with increasing pressure, and an increase with increasing temperature. The familiar conception of a liquid due to van der Waals is competent to explain this. The difference between the free space open to the molecules for their temperature vibrations and the total volume of the liquid is equal to the volume of the molecules themselves, or else to a small multiple of it. When pressure is increased, therefore, the free space diminishes much more rapidly than the total volume. Now we may suppose the pressure exerted by a liquid to be due in large measure to the bombardment of the walls by the temperature agitation of the molecules. The more frequent the collisions, the greater the pressure. Now at constant temperature, the number of collisions is inversely as the free space. At higher pressures, that is smaller volumes, a given diminution of total volume implies a greater diminution of the free volume than at low pressures, and therefore a greater increase of pressure. So that at small volumes (high pressures) a given decrease of volume carries with it a greater increase of pressure than at larger volumes (lower pressures), or in other words, the compressibility decreases with rising pressure. The increase of compressibility at higher temperatures is to be explained in the same way. At higher temperatures (constant pressure) the volume is greater and we expect greater compressibility. This however, is not the only element involved in the change of compressibility with temperature; there is also a temperature effect as such. It was found in the paper on water that, at equal volumes, the compressibility was always less at the higher temperatures. The reason is evidently the more rapid agitation of the molecules. At equal volumes, a given decrease in the total volume, and so of the free volume, will produce the same proportional increase in the number of impacts at high and low temperatures, but at high temperatures each impact involves a greater change of momentum, with the result that at the higher temperatures a given decrease of volume produces a greater increase in pressure, which means a lower compressibility.

A detailed examination of the curves shows that these expectations are justified to a rather greater degree than was the case for the thermal dilatation. The compressibility decreases with rising pressure for all twelve liquids at 40°. A careful analysis of the difference

curves will show that this is also the case for the other three temperatures, with a single exception. For carbon bisulphide, between 11000 and 12000 kgm. there is an increase of compressibility from 0.0_3101 to 0.0_3102 at 60°, and from 0.0_3103 to 0.0_3105 at 80°. The change is very small and may well be due to experimental error. The difference curves show as bewildering small variations with temperature as the thermal dilatation curves, so that it is hopeless to try to explain them in detail at this stage of our knowledge. It would seem, however, that an actual reversal of the effect, that is, a smaller compressibility at a higher temperature, does not occur so often as was the case for the dilatation. The reversal of the dilatation was universal for all liquids and took place between 1000 and 3000 kgm. But the reversal of the compressibility, indicated by the difference curve crossing the axis, is sporadic in occurrence, and only once occurs for all temperatures simultaneously.

Comparison of the curves shows some points of interest. The first three alcohols show a slight kink; propyl alcohol at 3000 kgm., ethyl at 1100, and methyl possibly at a somewhat lower pressure. Amyl alcohol apparently has lost the kink. These four alcohols show in rather desultory fashion for at least one temperature the temperature reversal at high pressures. Isobutyl alcohol, as we expect, shows the effect of structural variation by curves of different character from the other four alcohols, in that they show no reversal, but decrease with fair regularity under increasing pressure. Isobutyl alcohol is also remarkable for the extremely rapid initial drop of compressibility with rising pressure. Ether, the isomer of isobutyl alcohol, still further shows the importance of the structure of the molecule; the difference curves for ether show reversal at high pressures, and are also more widely separated than the curves for isobutyl alcohol. The last six liquids show a somewhat greater temperature effect on compressibility than the first six. Acetone shows a strange maximum in the difference curve between 4000 and 5000. Carbon bisulphide shows greater variations at the highest pressures than any other liquid (it will be remembered that the dilatation curves also show abnormally great variations), and a reversal of the effect at 9000 kgm. simultaneous for all temperatures. This simultaneous reversal is shown by no other liquid, and reminds one of the dilatation. Phosphorus trichloride shows no marked features; the compressibility curves are not so simple as the dilatation curves. The halogen compounds do not show any marked similarities. Ethyl chloride is without particular features. Ethyl bromide has a very pronounced

separation of the curves for 20° and 40° at 4000 kgm., while ethyl iodide shows a similar, but smaller separation between the 20°–40° and also the 40°–60° curves. The halogens all show reversals at the high pressures.

The occasional reversal of compressibility with temperature, that is, a smaller compressibility at a higher temperature, has ready explanation if we adopt the hypothesis of molecules with shape. We have seen that in this event, because of the varying completeness with which the molecules interlock, it may sometimes happen that the increase of volume with temperature results in a decrease of the free space open to the thermal agitation of the molecules. In this case the compressibility is less at high temperatures than at low. The same argument would admit also the possibility of compressibility increasing with increasing pressure if the effect of pressure is to produce a better fitting together of the molecules and so greater free space. It may be, therefore, that the effect found for carbon bisulphide is genuine, and not to be explained away by experimental error.

As a general rule, the result found for water applies to these twelve liquids also, namely that compressibility when plotted against volume is less at the higher temperatures. There are, however, a few exceptions. Carbon bisulphide and ethyl chloride, for example, show a reverse effect at the higher pressures. A possible explanation of this is to be found in the opposition of two effects. In general we think of the effects of lowering the temperature and of increasing the pressure as the same, namely to increase the degree of interlocking of the molecules. If now we compare two states of the liquid, each occupying the same volume, but one at a higher temperature than the other, we see that the high temperature condition differs from the low in that the molecules are less interlocked so that they have less free space at their disposal. An increase of pressure will tend to produce a smaller change of volume at the high temperature therefore, because of the smaller free space which the molecules possess. But on the other hand, an increase of pressure will tend to produce a greater change of volume because the effect of increased pressure is to increase the amount of interlocking, and so to decrease the volume. As one or the other of these effects predominates, we shall have smaller or greater compressibility at the higher temperatures with constant volume. We have seen that the compressibility is usually smaller.

We turn now to the diagram (Figure 45) in which are collected

the average of the results for all twelve liquids. As for the curves of thermal dilatation, the zeros of the successive curves are displaced

TABLE XIX.

CHANGES OF COMPRESSIBILITY AND THERMAL EXPANSION PRODUCED BY PRESSURE.

Liquid.	Compressibility, κ.				Dilatation, δ.			
	$\frac{\kappa_1}{\kappa_{12000}}$	$\frac{\kappa_{1000}}{\kappa_{12000}}$	$\frac{\kappa_{6000}}{\kappa_{12000}}$	κ_{12000}	$\frac{\delta_1}{\delta_{12000}}$	$\frac{\delta_{1000}}{\delta_{12000}}$	$\frac{\delta_{6000}}{\delta_{12000}}$	δ_{12000}
1	18.4	8.2	2.20	$0.0_5 74$	4.29	2.76	1.23	$0.0_3 298$
2	13.7	7.4	2.02	81	4.50	2.73	1.30	268
3	15.8	7.8	1.94	70	4.80	3.06	1.33	237
4	16.6	6.3	1.68	86	4.15	2.62	1.17	275
5	14.4	7.1	1.88	74	4.40	2.84	1.30	240
6		7.7	1.62	96		3.65	1.32	248
7		7.3	1.85	87		3.27	1.35	282
8	13.8	6.3	1.82	87	5.47	3.16	1.31	262
9	14.2	7.1	1.81	80	4.84	2.83	1.31	278
10		8.4	1.78	90		3.44	1.37	267
11	14.9	8.3	1.87	82		3.46	1.33	260
12	14.9	7.2	1.89	81	4.86	3.15	1.22	248
Water	4.9	3.7	1.64	89	1.00	1.00	1.00	400
Kerosene			1.82	87			1.14	280

one square with respect to each other. The origin of each curve is so situated that at 12000 kgm. the compressibility has approached to within less than one unit of zero. Thus, the compressibility of ethyl alcohol at 12000 is $0.0_5 81$.

The most striking feature is that the curves become nearly equispaced at the higher pressures. This appearance of increasing equality of behavior is not an illusion due to the approach of all the curves to

zero, but it is real, as shown by the fact that the variation in the ratios of the initial compressibilities of the liquids to each other is greater than the variation in the ratios at 12000 kgm. The increasing equality at high pressures is also made more strikingly visible to the eye by noting on the diagram at what pressure the compressibility is equal to $0.0_{4}20$. For all the twelve liquids except propyl, isobutyl, and amyl alcohol this pressure is between 4000 and 5000 kgm., and for the alcohols it is not far removed. This is the same sort of thing that we have seen to hold for the dilatation curves.

The compressibility curves are, however, quite different from the dilatation curves in several respects. The effect of pressure is very much greater in decreasing the compressibility than in decreasing the dilatation. Furthermore, the decrease of compressibility at the higher pressures continues to be more rapid than that of the dilatation; both the initial and the final relative rates of change are more rapid for the compressibility than for the dilatation. This is shown in Table XIX. In the second and sixth columns of this table the relative changes of compressibility and dilatation are given over the entire pressure range. The change is about four times greater for the compressibility than for the dilatation. The fourth and eighth columns show that the change between 6000 and 12000 is greater for the compressibility than for the dilatation. In other words, the dilatation comes much nearer to approaching a finite asymptote than the compressibility. This is not what was expected at first. It was thought that at high pressures the molecules would be squeezed into virtually perfect contact, that the compressibility would be provided for by the compression of the molecules, but that under these conditions the dilatation would practically vanish. The exact reverse has turned out to be the case. The data previously obtained for water and kerosene have also been included in the table. At high pressures kerosene behaves much like the other liquids. Water is nearly normal at high pressures as regards compressibility, but is abnormal over the entire range with respect to temperature effects.

The compressibility of these liquids at 12000 kgm. may be compared with the compressibility of metals under ordinary conditions. For mercury the value is about $0.0_{5}39$, and for iron $0.0_{6}58$. The average compressibility of these liquids at 12000 kgm. is therefore, about twice the initial compressibility of mercury and about fourteen times that of iron. The average dilatation at 12000 approaches more nearly to that of mercury, being about 40% greater, but is farther

removed from the dilatation of iron, being about 20 times greater. The difference between compressibility and dilatation is further accentuated by the fact that the compressibility of iron is nearly as low as that of any solid, while there are a number of solids with a smaller dilatation. There seems, therefore, to be more difference between a solid and a liquid with respect to thermal expansion than with respect to compressibility.

Pressure Coefficient.— No diagrams have been given for this quantity, but it is nevertheless worth some discussion, because of the part it has played in previous theoretical discussions. This so-called "pressure coefficient" is the thermodynamic quantity $\left(\frac{\partial p}{\partial \tau}\right)_v$, the change of pressure when the temperature is raised one degree at constant volume, and is mathematically equivalent to the ratio of dilatation to compressibility $\left(\frac{\partial p}{\partial \tau}\right)_v = -\left(\frac{\partial v}{\partial \tau}\right)_p \Big/ \left(\frac{\partial v}{\partial p}\right)_\tau$. It has been proposed as an empirical law by Ramsay and Young that the pressure coefficient is a function of the volume only. That is, if the pressure coefficient is plotted against volume, the curves for different temperatures will fall together. The experiments of Ramsay and Young covered a wide temperature range, but a comparatively low pressure range, since their chief concern was with the relations between a liquid and its vapor, and their pressures seldom exceeded the critical pressure, a matter of a few hundred atmospheres. Amagat, in his discussion of his own results for liquids up to 3000 atmos., has devoted considerable attention to the pressure coefficient. One of his results was that the pressure coefficient is approximately independent of temperature at constant volume, but does nevertheless show small consistent variations, which Amagat was unwilling to ascribe to experimental errors. The coefficient of different substances may increase or decrease with rising temperature, or show still more complicated variations. The coefficient increases with decreasing volume, that is with increasing pressure. Tammann, however, in his recent empirical theory of liquids for high pressures, has concluded from an examination of Amagat's work that the variations which Amagat found in the pressure coefficient do not exceed the possible experimental errors. Tammann has accordingly taken as one of the fundamental hypotheses of his theory the assumption that the pressure coefficient is a function of the volume only.

The discussion of the pressure coefficient to be given here has for its only purpose to show that at high pressures, whatever the facts

may be at low pressures, there is absolutely no ground for the assumption that the coefficient remains independent of the temperature. This was shown to be the fact in the previous paper on water, but the argument lost force because water is abnormal. However, for none of the twelve liquids of this paper is the relation even approximately

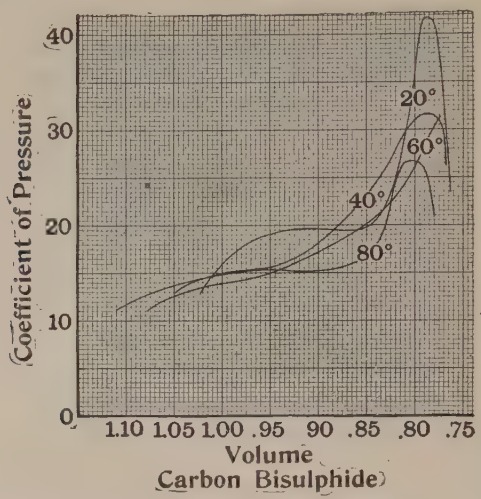

FIGURE 46. The pressure coefficient of carbon bisulphide plotted against volume. The diagram shows that at high pressures the pressure coefficient is a function of temperature as well as of volume.

satisfied. It is not necessary to show curves for all twelve liquids in order to disprove this one point. The data are at hand so that any one may make a complete test for himself. A single diagram, chosen at random, is sufficient to show that the proposed relation breaks down completely, as indeed one would expect it to in view of the complications of compressibility and dilatation. Figure 46 shows this for carbon bisulphide. It speaks for itself.

Work of Compression.— The mechanical work of compression is shown in Folder III; Figures 47 to 58 are for the liquids separately, and Figure 59 shows the average between 20° and 80° of all twelve liquids together. The difference of the work for different temperatures is so nearly the same that the differences could not have been read accurately directly from the curves. The course was adopted, therefore, of plotting the work at 40° only, and in the lower

part of the diagram giving on an enlarged scale the difference of the work for intervals of 20°.

The curves for the separate liquids do not require much comment. The difference curves are universally positive; that is, it is always true that more mechanical work is expended when a liquid is compressed to a given pressure at a high temperature than at a lower one. Beyond this, however, there do not seem to be many common features. The curves show irregular and apparently unrelated variations, but the irregularities are not so great as for the dilatation or the compressibility. Of course this was to be expected, because the curves are essentially integral curves.

Three of the alcohols, methyl, ethyl, and amyl, show similar difference curves. Ether and isobutyl alcohol, isomers, are unlike, as we have found them before. The difference curve 20°–40° for carbon bisulphide shows the effect of the abnormally high compressibility at 20°, which we saw previously, and the three ethyl halogens show similarities. Other variations in the difference curves are not particularly illuminating.

Figure 59, combining the average results for the twelve liquids, is of more interest. The similarity in general shape of all the curves is perhaps the most interesting feature. The curves become nearly linear at the higher pressures. This of course is not the usual relation between stress and work for a body like a steel spring, which maintains a stiffness independent of stress. For such bodies the work stored up as potential energy of strain varies as the square of the stress. This is true for liquids also over a pressure range so small that the compressibility may be regarded as constant, and is shown in the initial stages by all the curves, which are tangent to the axis at the origin. The fact that at high pressures the curves tend to become linear, still remaining slightly concave upwards, means that at high pressures the compressibility is becoming less, so that the change of volume, and therefore the work, is less for a given increment of pressure.

If we assume tentatively that the work of compression is linear at high pressures, we have a means of finding the compressibility and the volume at high pressures. For;

$$W = -\int_1^p p\left(\frac{\partial v}{\partial p}\right) dp = a + bp \quad (a \text{ is negative, } b \text{ positive}).$$

Differentiating this equation, we obtain,

$$\left(\frac{\partial v}{\partial p}\right)_t = -\frac{b}{p}$$

whence,

$$\Delta V = \int^{p} \left(\frac{\partial v}{\partial p}\right)_t dp = -b \log p + C.$$

This equation cannot be expected to hold for low pressures. The constants may be determined as follows. From the curves for W above 5000 kgm. we find that an approximate value for b is 0.1. If furthermore we assume as a fair average of all twelve liquids that $\Delta V = -0.25$ when $p = 5000$, the equation becomes,

$$\Delta V = -0.1 \log_e p + 0.6017.$$

The equation evidently cannot hold for infinite pressures, because it demands that ΔV decrease indefinitely, and it is physically impossible that ΔV should become less than -1. But the pressure at which this would happen according to the above formula is 9,060,000 kgm. This is so very far beyond the range of these experiments, that it would probably be safe to apply a similar equation as an approximate expression for any experimental pressures above 5000 kgm.

The mathematical analysis gives us, furthermore, information as to the ultimate behavior of the work of compression. For the actual work must eventually be less than that given by the above formula, which corresponds to a smaller change of volume. It must be, therefore, that at higher pressures the curvature reverses, and the curve becomes convex upwards. Methyl and amyl alcohol show the beginning of this effect, but in view of the extreme remoteness of the vanishing of the volume predicted above, it may well be that this slight change of curvature is merely one of the many local variations.

The maximum amount of work stored up at 12000 kgm. is nearly the same for all twelve liquids; much more nearly equal than the initial differences in the compressibilities would lead us to expect. The variations in the maximum are about 25%, whereas there are initial variations in the compressibility of 100%. If we admit water to our family of curves, as we may because the final work of compression is over 9 kgm. m., the variation in the initial compressibility may be 400%. Initial differences of compressibility have little effect on the work at the maximum pressure, because of the comparatively small amount of work done at low pressures.

The total amount of mechanical work stored up in a liquid is quite considerable. For example the work of compression of ether at 12000 kgm. would suffice to raise it through about 45000 ft., or to give it a velocity of 1700 ft. sec.

Heat of Compression.— The heat of compression, that is the quantity of heat in kgm. m. which flows out of a substance as it is compressed isothermally, is shown in Folder 4; for the twelve liquids separately in Figures 60 to 71, and the average for the twelve liquids collected into a single diagram in Figure 72. The differences of the curves for different temperatures are sufficiently great so that the total heat of compression for each temperature could be plotted and the difference found with sufficient accuracy directly from the curves, without the necessity of drawing difference curves as was the case for the work of compression. The zero of each curve has been displaced upwards one square for the successive temperatures. In the case of those liquids which boil at low temperatures, the zero of the curves for all temperatures has been taken at the same pressure, 500 or 1000 kgm., although it would have been possible to extend the curves to atmospheric pressure for the lower temperatures. In the case of acetone and ethyl chloride the curves for the lower temperatures have been extended backwards from the origin (1000 kgm.) to atmospheric pressure.

The heat of compression is positive, that is, as a substance is compressed isothermally, heat flows out to the surroundings. Examination of the curves in detail shows also that the total heat always increases with increasing pressure. This is a direct consequence of the fact that the thermal expansion is always positive. The curves therefore, show less pronounced irregularities than some, such as those for compressibility for example.

In general, the concavity is toward the pressure axis, that is, the increase of the heat of compression becomes less rapid at the higher pressures. The curves for the different liquids at different temperatures show that the heat is not universally greater at the higher temperatures, although such is generally the case. This is shown by the curves drawing together at high pressures in some cases to within less than the one square which separated them at the origin. An example of this is afforded by amyl alcohol between 20° and 40°, and by ethyl chloride and ethyl iodide between 60° and 80°. In general, a drawing together of the curves with increasing pressure means that the expansion is less at the higher temperature. There are many instances of this, although it is not usual that the drawing together is great enough to bring the curves to within less than the original arbitrary distance of separation.

Figure 72, in which are collected the average results for all twelve liquids, shows again that the twelve liquids are alike in character.

It is true that the curves cross in one or two instances, and are unevenly spaced at the high pressures, but the differences are very much

TABLE XX.

COMPARISON OF THERMAL EXPANSION WITH HEAT OF COMPRESSION.

Liquid.	Expansion.		Heat of Compression	
	Expansion at Atmospheric Pressure.	Ratio to Average.	Heat at 12000 kgm.	Ratio to Average.
1	.00128	.91	18.0	1.04
2	120	.85	16.4	.95
3	115	.82	18.0	1.04
4	114	.81	16.0	.92
5	106	.75	14.9	.86
6	170(?)	1.20	17.4	1.01
7	172(?)	1.22	19.6	1.13
8	143	1.01	18.0	1.04
9	134	.95	17.5	1.01
10	190(?)	1.35	18.5	1.07
11	185(?)	1.31	18.3	1.06
12	120	.85	15.5	.89
Average	141		17.3	
Maximum variation of initial expansion, 1:1.8 Maximum variation of heat at 12000 kgm. 1:1:3				

less than one would expect from the differences in the initial direction of the curves. The heat of compression is given by $Q = \int \tau \left(\frac{\partial v}{\partial \tau}\right)_p dp$, so that the relative initial values of $\left(\frac{\partial v}{\partial \tau}\right)_p$, that is the initial slopes

of the curves for Q, give us an idea of what we might expect to be the relative values of Q if the liquids preserved over the entire pressure range their relative initial behavior. Table XX shows this. It gives the initial dilatation and its ratio to the average, the total heat given out at 12000 kgm. and its ratio to the average. The dilatation tabulated for the low boiling liquids was obtained by a linear extrapolation, which gives values too small. Larger values for these liquids would only increase the force of the argument. It is obvious that the two ratio columns show only a general rough agreement; large values of one corresponding to large values of the other. There seems to be no correspondence in the small variations in the ratio column. This shows that the initial behavior of a liquid with respect to the heat of compression does not fix its behavior at the higher pressures. Furthermore, the magnitude of the variations in the ratios of the dilatation are greater than the variations of the heat ratios; a maximum variation in the one column of 1:1.8 against 1:1.3 in the other. This shows again that the liquids become more alike at the high pressures than we should expect from their initial behavior at atmospheric pressure.

The magnitude of the heat of compression is of interest. For the average liquid this is about 17 kgm. m. at 12000 kgm. If we take as a fair average for C_p 25 kgm. cm. this means that the amount of heat flowing out of the average liquid as it is compressed isothermally to 12000 kgm. would raise it through 68° at atmospheric pressure.

Change of Internal Energy. — This quantity is shown on Folder V; for the twelve liquids separately at four temperatures in Figures 73 to 84, and the average results for the twelve liquids plotted against pressure in Figure 85 and against volume in Figure 86. The change of energy plotted in these figures is the internal energy at atmospheric pressure minus the internal energy at the pressure in question. A positive value for the change means, therefore, that the internal energy is less at the higher pressure than it is at atmospheric. The origins of the curves for the separate temperatures have been displaced with respect to each other, so as not to confuse by over lapping. In the cases where the liquid boils at low temperatures the origin of the curve for the higher temperatures has been taken at 500 or 1000 kgm.

The change of internal energy was found by taking the difference between the heat and the work of compression. The curves show nothing, therefore, not already given.

The different substances show irregularities which cannot be dwelt

on here. In general, the curves for the higher temperatures tend to draw apart, that is, the decrease of internal energy is greater at the higher temperature, but there are several well pronounced exceptions to this rule. Amyl alcohol, ethyl chloride, and ethyl iodide, for example, are exceptional at the same temperatures where we found exceptional behavior with respect to the work of compression.

The change of internal energy is to be thought of as brought about by the counterplay of two opposing sets of forces, and it is significant because of what it can tell us about these forces. When a substance is compressed, the molecules are brought closer together, the attractive forces between the molecules do work, the potential energy of the attractive forces decreases, and the internal energy decreases. But at the same time, the molecules become compressed by mutual contact, energy is stored up inside the molecule by the external forces in the form of potential energy of strain, and the internal energy increases. Now these two sets of forces play very different roles at different stages of the compression. At low pressures, where the molecules may be thought of as possessing a free path, no potential energy of strain can be permanently stored up in the molecule, because during the motion in the free path it has been entirely converted into translational kinetic or temperature energy. This is what takes place in a gas. But as the volume of the liquid becomes less, the length of the free path rapidly becomes smaller, and at any instant an increasingly large number of molecules is not describing part of any free path at all, but is merely being handed on directly from one collision to the next. At this stage, potential energy of strain can be permanently stored up within the molecule. At still higher compressions, when the molecules are practically in continuous contact, there is still greater possibility of storing up internal energy of strain. The possibility is limitless, provided only that the molecule never becomes incapable of further compression. The loss of internal potential energy by the attractive forces cannot proceed beyond a certain limit, however, imposed by the least distance of approach of the molecules.

We should expect, therefore, that at low pressures the internal energy would decrease with rising pressure, the attractive forces being in the ascendant, but at the higher pressures, where the forces resisting compression have become dominant, that the energy would increase with rising pressure. For the two liquids previously investigated in this respect, mercury and water, the energy was found to continue to decrease over a pressure range of 12000 kgm. The direc-

tion of curvature was in each case such as to suggest that this decrease might not continue indefinitely, and it was suggested then that there must ultimately be a reversal of the effect. It seemed surprising that at pressures as high as 12000 kgm. the attractive forces should still do more work than could be stored up as strain by the external forces.

Figure 85, giving the average for the twelve liquids, shows that the anticipation of a reversal in the change of energy is justified for nearly all the liquids; that is, the internal energy, after decreasing for a while, passes through a minimum (on the curves a maximum) and from here increases with rising pressure. The necessary existence of this maximum could of course have been predicted from the curves for the heat and the work of compression, since the one is either linear or concave upwards, while the other is concave downwards.

The change of energy is markedly different for the different liquids, whereas the other thermodynamic properties are similar. Of course the reason is that we are here concerned with the difference of two effects. The position of the maximum of the difference of two functions is very sensitive to slight changes in the functions themselves. Under these circumstances, the mere existence of a maximum is evidence of similarity. The only curves which do not show the maximum are methyl and propyl alcohol. It will be remembered that the work of compression curve for methyl alcohol had a reversed curvature at the upper end, and that the work of compression of propyl alcohol was abnormally low.

It is of interest to plot the change of energy against volume, because it may give information about the attractive forces. If the attractive forces are central forces, functions only of the distance from the centers of the molecules, then the potential energy of the attractive forces will be a function of the volume. Thus if the attractive forces are proportional to the inverse fifth power, as has often been supposed, then the potential energy is inversely as the fourth power of the distance apart of the molecules, or as the inverse four thirds power of the volume. This relation was tried for four of the twelve liquids; for amyl alcohol, ether, phosphorus trichloride, and ethyl iodide. The change of internal energy of these liquids was plotted against $V^{-\frac{4}{3}}$. The diagram was the same in character as the diagram plotting the change of energy against V, except of course that small values of $V^{-\frac{4}{3}}$ correspond to large values of V. Now if the change of internal energy is proportional to $V_0^{-\frac{4}{3}} - V^{-\frac{4}{3}}$, this curve plotted against $V^{-\frac{4}{3}}$ should be linear. The curves were very nearly linear in the in-

itial stages, but of course ultimately diverged greatly from linearity, passing through a maximum. If the straight portion of the curve at the origin represents a region in which the inverse four thirds power law is satisfied, then the tangent to the curve at the origin represents over the entire range of the experiment what the change of energy would have been if the four thirds law had held throughout. The difference between the actual curve and the tangent at the origin is then, according to the above view, equal to the energy which has been stored up as strain inside the molecule. This difference was determined and plotted against volume, in order to find what function of the volume the strain energy might be. For these four liquids, it turned out that the strain energy varies over the entire range approximately as the cube of the change of volume reckoned from a suitable origin. The greatest discrepancy is for ether at low pressures. For PCl_3 a variation of only 0.01 in the arbitrary zero of volume from which the change is reckoned would wipe out the discrepancy; for amyl alcohol a variation in the zero of 0.005 would give perfect agreement; for ethyl iodide a change of 0.01, and for ether a change of 0.04. The variation for ether is all below 3000 kgm.; above this the energy of strain is almost exactly proportional to the cube of the change of volume, taking 1.06 as the origin. The zero of volume for phosphorus trichloride is 1.11, for amyl alcohol 1.07, and for ethyl iodide 1.045. All the curves showed slight consistent variations from the cube law; at low pressures the strain energy varies more rapidly than the cube and less rapidly at the high pressures.

The fact that the internal energy of strain varies as the cube of the change of volume probably does not have very much significance in showing us what the elastic mechanism of the molecule is. If the entire change of volume of the liquid were due to change of volume of the molecules, then we should expect the strain energy to vary as the square of the change of volume, provided the elastic constants of the molecule were unaffected by pressure. If, as is likely, the molecule becomes less compressible at high pressure, then the strain energy would vary less rapidly than the square. But the strain energy was found to vary as the cube. The reason for this is probably that at low pressures strain energy is stored up in only a few of the molecules; those molecules which are describing a free path and are not in contact with other molecules have no strain energy of compression. With increasing pressure the number of molecules in which strain energy is stored up increases rapidly, and the strain energy of each molecule increases at the same time as the square of the strain.

so that the total energy of strain would be expected to increase more rapidly than the square of the change of volume, as we found it to. But any more detailed speculation as to the precise way in which the number of molecules taking part in the strain, and the way in which the strain energy of the average molecule varies with the total pressure, would probably be useless because the argument as to the attractive forces breaks down at small volumes. It is probable that the molecules are not really homogeneous spheres, but that there are localities in which the attractive forces are more or less concentrated. Therefore, although we may regard the attraction exerted by the molecule as toward its center, and inversely as the fifth power of the distance when the molecules are separated by wide intervals, we cannot conceive of this law continuing to hold when the molecules are so close as to be in contact. Under these circumstances the force may increase more rapidly than as the inverse fifth power. What is more, the potential energy of the attractive forces will not under these circumstances be a function of the volume only, that is of the mean distance apart of the centers of the molecules, but will also vary with the orientation. We saw that the average orderliness of orientation may be expected to vary with temperature, being on the whole more haphazard for equal volumes at the high temperatures. Even with this picture of what is happening, it would be difficult to say whether the potential energy of attraction should be expected to be greater at the higher or lower temperature. We have seen that the lower temperature usually means a greater space open for occupation, but it may still be that because of the greater approach to order at the low temperatures the localities of intense force are brought closer together, so that the potential of the attractive forces may be less.

The main conclusion to be drawn from the fact that the strain energy of the molecules varies as the cube of the change of volume is, therefore, that at low pressures the greater part of the change of volume is due to the decrease in the distance apart of the molecules, but that at high pressures an increasingly large part of the change of volume is occasioned by the actual change of volume of the molecules themselves.

It is interesting that the initial slopes of the curves of change of energy against volume are very nearly the same for all twelve liquids. This is a little unusual. Previously we have found the twelve liquids to become similar at high pressure, but in respect to the change of energy they appear to be more alike at low pressures.

Specific Heat at Constant Pressure.—The specific heat at constant pressure is shown on Folder VI; the curves for the twelve liquids at four temperatures in Figures 87 to 98, and the collection of the average results in Figure 99. The quantity listed as change of C_p is the specific heat at atmospheric pressure minus the specific heat at the pressure in question. A positive change means, therefore, that the specific heat is less at the pressure in question than at atmospheric pressure. In order not to confuse the curves, the origin for each temperature has been displaced with respect to the neighboring curves. The scale of the drawing is shown at the right hand side.

The twelve liquids show a bewildering variety, so bewildering that speculation as to the cause of all the variations is hopeless. It is to be pointed out nevertheless, that such great variety is to be expected if the molecules take up different positions more or less symmetrical in arrangement with increasing pressure. The process is similar in many ways to a process of association, which is accompanied by much greater changes in the specific heats than in the volume, or compressibility, or dilatation. The curves show some points of similarity, however. It is an almost universal rule that the initial change of C_p at any temperature is a decrease. For the majority of liquids the specific heat on the whole decreases at the high temperature and increases or does not increase so much at the low temperatures. We have seen that as a rule the specific heat at atmospheric pressure is higher at the higher temperatures. For some liquids the temperature effect may be very marked. The change under pressure is in such a direction as to bring the specific heats at high pressures more nearly to equality for all the temperatures. The three halogen compounds are an exception to the rule, however. The very large increase of C_p for ethyl chloride at 80° is very much like that already found in the case of water. It may mean an abnormally high rate of dissociation at the higher pressures. The four normal alcohols show similarities in the abnormally large decrease of C_p at 80°. The decrease evidently cannot go on indefinitely. For methyl and ethyl alcohol, the maximum pressure is sufficient to change the decrease into an increase, as it must eventually, but for propyl and amyl alcohols, the reversal in direction must be at higher pressures than reached here. It seems to be at hand for propyl alcohol.

There is one very rough check which may be applied to the values given here for the specific heats; namely, in no case must the specific heat decrease by an amount more than its original value, for a nega-

tive specific heat is impossible. The only case where this condition comes anywhere near making trouble is for amyl alcohol. The curve for 80° shows a decrease of C_p of 21 kgm. cm. The data for atmospheric pressure are discordant, but 25 kgm. cm. seems to be a fair average value at 80°. This would mean that the specific heat at 80° and 12000 kgm. is only 4 kgm. cm., about one sixth its initial value. It is evident that the reversal in the effect must come speedily.

Figure 99 for the average change of C_p over the entire temperature range for the twelve liquids shows much less variation from liquid to liquid than one might expect from the irregular variations at the different temperatures. The curves in general all show the same characteristics; at first a decrease of specific heat and then an increase at higher pressures. The first minimum has already been commented on in another connection. Beyond this minimum in C_p (maximum on the curves) there is in general a continuous increase with rising pressure, although there are several cases where C_p decreases again slightly at the highest pressures. The three halogen compounds are exceptional (and also acetone) for the rather large increase of C_p with rising pressure. The increase is greater for the heavier members of the series.

The data of the previous paper on water show the same behavior, a minimum in C_p for all temperatures (except at 0° where the curve is broken off by the freezing) and then an increase with still further increasing pressure. The pressure for the minimum is higher than for these twelve liquids because of the abnormal behavior of water at low pressures.

So far as is known to the author, these are the only measurements from which an attempt has been made to find the specific heat at high pressures. The probable behavior of the specific heats does not seem to have been suspected. Thus Tumlirz deduces from his empirical equation for liquids that both the specific heats decrease with rising pressure. For water, Tumlirz finds the limiting value of C_p for infinite pressure to be about 0.5 gm. cal. He does not compute it for the other liquids. We see from the above that we are to expect for all liquids an ultimate increase instead of a decrease with rising pressure.

Specific Heat at Constant Volume. — The specific heat at constant volume is shown in Folder VII, the curves of the different liquids at different temperatures in Figures 100 to 111, and the collected averages for all the liquids in Figure 112. The treatment of these curves is the same as for C_p.

The curves are the same in general character as those for C_p. The differences consist in displacements of the pressures of maximum or minimum, or occasionally in the suppression of small irregularities; but the larger features are the same. The curves for the four normal alcohols retain the same resemblances as before, and isobutyl alcohol is as strikingly not a member of the series. Isobutyl alcohol and ether show general resemblances as to the specific heat, which may, however, be accidental. The halogens are also different from the other liquids with respect to C_v.

The importance of tabulating C_v is that it is a quantity of much greater simplicity than C_p. When we determine C_p by heating the liquid at constant pressure, the liquid expands with rising temperature, and in so doing performs work against both the external pressure and the internal attractive forces. C_p is greater than C_v by this work against external and internal forces. Consequently, it is usual to tacitly assume that C_v contains only the work necessary to raise the temperature energy of the molecules. Evidently the assumption is merely another way of stating the assumption that the potential energy of the attractive forces is a function of the volume only. Furthermore, it is usually assumed in discussions of the significance of C_v that a given increase of temperature corresponds to a given increase of kinetic energy of the molecule, no matter what the pressure of the liquid. It is true that when the kinetic energy of the molecule is to be raised, more total energy must be imparted to the molecule than just sufficient to increase the kinetic energy by this amount, because of the law of the equipartition of energy among the various degrees of freedom, but if the degrees of freedom remain unaltered, we still have the result that to increase the temperature by a given amount requires the same amount of work independent of the volume. The consequence of the hypothesis would be that the specific heat at constant volume is independent of pressure and temperature.

Figure 112 for the average C_v of the twelve liquids, shows that even on the average C_v cannot be independent of pressure, and the preceding diagrams for the separate liquid show that it certainly cannot be independent of temperature. In general the behavior of C_v seems to be at first a decrease, and then with increasing pressure an increase again. Probably the reason is that neither of the simple hypotheses which we discussed above are valid for high pressures. We have seen that at high pressures we may expect the molecules to approach positions of more or less regularity of arrangement, and that the regularity is greater at the low temperatures. Now according to the

particular arrangement which the molecules adopt, and the relation of the local centers of force to this arrangement, it is conceivable that the potential of the attractive forces should be either greater or less at the lower temperatures and equal volumes. The likelihood is, however, that the potential will usually be less at the lower temperatures. Similarly, it is usually more likely that the potential of the attractive forces should be less at the higher pressures. As a rule, then, an increase of temperature of one degree at a higher pressure or a lower temperature must provide the energy to do more work against the attractive forces, so that the specific heat at constant volume will be greater at higher pressure and lower temperature. But in those more infrequent cases where the potential energy of position is less at the higher temperature or lower pressure, the specific heat will be less at higher pressures and lower temperatures. It is as a rule true, as we have seen from the curves, that C_v does become greater at the higher pressures and lower temperatures.

The considerations just discussed are somewhat similar to considerations regarding the association of the molecules, but do not in all cases lead to the same results. For instance, if we suppose a liquid of single molecules to associate to one of double molecules, the specific heat of the associated liquid would be one half that of the simple one, if we neglect the effect of the altered number of internal degrees of freedom.

The second hypothesis made above, that a given increase of temperature always corresponds to the same increase of molecular energy, probably breaks down also at high pressures. The difficulty of determining what happens in this case is increased by uncertainty as to what the definition of temperature shall be at high pressures. We may perhaps, however, think of temperature at low pressures as being roughly proportional to the average translational energy of the molecule during its free flight. Now we have seen that as pressure increases, the time of free flight decreases rapidly, and an increasing fraction of the time is spent in collision. During collision the kinetic energy of translation has become potential within the molecule. The result is that as pressure increases, the potential strain energy of the molecules becomes a greater part of the total energy, leaving a smaller residue to become kinetic. Now if temperature corresponds to translational kinetic energy, it is evident that at high pressures more total energy must be imparted to the substance to increase the translational energy a given amount, or in other words, the specific heat will increase with increasing pressure.

The initial decrease of C_v may very possibly be an association effect. A word should be said about this association effect. The reason that an association from single to double molecules, for example, reduces the specific heat to one half, neglecting the effect of the internal degrees of freedom, is that a rise of temperature of one degree corresponds to a definite increase in the kinetic energy of each molecule, and when there are half as many molecules, half the additional energy is needed to increase the energy by an amount corresponding to one degree. This means that association has an effect on specific heat as long as temperature remains a molecular affair. This is true for a gas. But the law of atomic heats for solids suggests very strongly that in solids temperature is no longer an affair of the molecule, but has become a matter of the atom. We naturally expect somewhere a transition from the one state to the other, and the liquid is the natural place to look for it. That is, if a liquid temperature is on its way from being an affair of the molecule to becoming an affair of the atom. It is not likely, therefore, that the existence of large molecular complexes in a liquid, as in the case of association, will modify very much the behavior with respect to temperature, and in particular to the specific heats. Such effect as there is should be looked for at low pressures.

A word should be said about the curves for the average of C_p and C_v over the entire temperature range. The average C_p is the total heat absorbed at constant pressure between 20° and 80° divided by 60. C_v is the average of the four values at 20°, 40°, 60°, and 80°. These two averages are not always equivalent when there are large variations with temperature, but they are always approximately equal. In cases of question, the average C_p corresponding to C_v may be found from the curves for C_p at the four temperatures. To find the average C_v corresponding to the average C_p would involve a more complicated procedure.

General Discussion of the Bearing of the Results on a Theory of Liquids for High Pressures.

It is proposed to discuss here the nature of the problems which confront one at high pressures. No attempt is to be made to develop a new theory, but merely to indicate some of the directions in which the data of this paper suggest modifications of conceptions which have hitherto worked at low pressures.

Perhaps the most far reaching modification is in regard to our

idea of the kinetic origin of pressure. We suppose that the pressure of a gas, for instance, is produced by the impact of the molecules against the walls of the vessel; and we compute the magnitude of the pressure from the total change in one second of the momentum of the molecules striking on unit area of the wall. The velocity with which the molecules strike the walls decreases with falling temperature and vanishes at the absolute zero. The pressure exerted by a liquid also is thought of in most attempts at a theory of liquids as exerted by the same mechanism and is computed in the same way. But it is entirely obvious that the molecules may exert pressure on the walls in another way. It is inconceivable that at the absolute zero a substance should not resist an attempt to compress it; yet at this temperature there can be no kinetic effect exerted by the molecules as a whole. Under these conditions the molecules transmit pressure in the same way that a compressed spring does; that is, they behave like elastic solids. It does not concern us here to inquire what the ultimate origin of this elasticity is; it may be kinetic within the atom. The point is simply this; from our point of view, which regards the molecule as a whole, we must recognize two possible functions or modes of action; the molecule may behave like a moving centre of mass with kinetic energy and momentum, or it may behave like an elastic solid. The molecule may exert pressure in virtue of either one of these two modes of action. Under ordinary conditions the momentum effect of its motion as a whole is almost the entire effect. But if we examine the mathematical analysis which justifies us in putting the pressure equal to the total change of momentum in unit time, we shall find that we made certain simplifying assumptions. We assumed that each collision with the wall is unimpeded; that is, the molecule approaches the wall during free flight, has a single encounter and makes a clean get-away. And this assumption was necessary; as soon as the molecule is interfered with during its collision, as it may be by a collision from another molecule from behind, the simple change of momentum relation ceases to give the pressure, and we must treat our molecule during collision as an elastic solid. Now it is evident that as the volume becomes less, that is, as the pressure increases, the total number of collisions with interference will increase, and our kinetic conception of pressure becomes less and less useful.

A very simple model, which may or may not correspond to the physical facts, is instructive in showing how under different conditions we may compute the pressure from the momentum effect alone, or must consider also the elasticity effects. The substance we are

to consider consists of a single molecule. The molecule consists of a heavy particle of mass m, with two weightless springs projecting on either side of length l_0, giving a total diameter of the molecule of $2l_0$. (Figure 113.) This molecule travels back and forth in a horizontal line between the two opposite vertical walls of the enclosure. The distance apart of the walls is the volume of the enclosure, the force exerted by the springs on the walls during an encounter gives the pressure exerted by the substance, and the kinetic energy of the particle at its maximum velocity represents temperature.

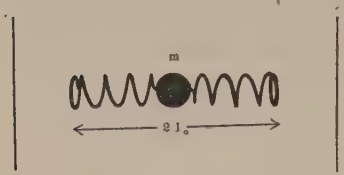

FIGURE 113. Model of a substance consisting of one molecule. The model is to show that at high compressions the pressure is not given by the change of momentum of the molecules striking the walls of the vessel in unit time.

This model is so simple that the entire discussion may be carried through with rigorous mathematical analysis. The pressure exerted on the walls is evidently to be found by taking the time average (over a long interval of time) of the force exerted on the walls by the springs during the encounters. Now in the solution of this problem there are three different cases.

I. The first case is when the distance apart of the walls of the vessel is greater than $2l_0$, the diameter of the molecule. Under these conditions we have collision without interference, which are the only conditions to which the usual analysis applies. In this case it may be proved by a detailed mathematical solution which will not be given here that the time average of the force is exactly equal to the change of momentum in unit time with respect to one of the walls, as it should be. The results of the mathematical analysis for this case may be given in the form of a distinctive equation of the substance,

$$P\,[(v - b) + a\,T^{\frac{1}{2}}] = 2\,T.$$

Here P is pressure, v = volume (distance apart of walls), b = diameter of molecule ($2l_0$), $a = \pi\sqrt{\frac{2}{k}}$, where k is elasticity of the springs, and T = absolute temperature (kinetic energy of particle). The equation bears a resemblance to van der Waal's equation without the attractive forces. In van der Waal's equation $a = 0$, or $\kappa = \infty$, which means that the time of collision of the particles with the wall may be neglected in comparison with the time of free flight.

II. The distance apart of the walls is less than $2l_0$, the diameter of

the molecule, and the kinetic energy of agitation is so small that at no time is the molecule out of contact with *both* walls simultaneously. The detailed mathematical solution shows that under these conditions the momentum effect has no influence whatever, and the pressure is determined simply by the relative magnitude of the volume and the unstressed diameter of the molecule. Under these conditions we obtain as the characteristic equation

$$P = \frac{k}{2}(b-v).$$

It is remarkable that the temperature has disappeared from the characteristic equation, or, in other words, the thermal dilatation is zero. The substance still remains compressible, however. Something like this was expected for the liquids of these experiments; that is, it was expected that the dilatation would tend to vanish more rapidly then the compressibility.

III. Case II passes into this case when the violence of the temperature vibration becomes so great that during part of the vibration the molecule is in contact with only one wall. The critical temperature at which this occurs is when $T = k\left(\frac{b-v}{2}\right)^2$. The mathematical analysis is more complicated for this case, because the motion must be split up into two stages, during which the restoring forces are different functions of the displacement. But just as in Case II, the change of momentum of the molecule in unit time does not give the mean pressure exerted on the wall. The complete equation of state for Case III is complicated, involving antisines, so that it is hardly worth giving. It reduces to one or the other of the other two cases, however, under proper critical conditions. In this case, the pressure computed by the change of momentum is too low, as we should expect it would be, because we have neglected an elasticity term which modifies conditions when the molecule is in contact with both walls.

The sequence of events when we compress a substance at a given temperature from a large volume is first Case I, then Case III, when $v = b$, and then Case II, when the volume has been still further reduced by an amount depending on the temperature. Case I passes smoothly into Case III without discontinuity in either compressibility or dilatation. The difference between Cases I and III is that a higher pressure corresponds to a given volume in Case III than we should expect from the formula of Case I. The pressure at a given volume in Cases I and III depends on temperature, but in Case II, the rela-

tion between volume and pressure is the same for every temperature. The only way in which temperature has an effect in Case II is with regard to the critical temperature which determines when Case II passes into Case III. The pressure for a given volume in Case III ultimately becomes less than we would have expected it to be if we extrapolated by the formula of Case I. In other words, the substance is more compressible than we should expect it to be from its behavior at low pressures. This reminds us of the formulas of Tumlirz and Tammann. It should be said however, that the mathematical analysis applied to Case III cannot continue to have physical significance indefinitely, for it was assumed that the springs obey Hooke's law, which is true only for small displacements. The characteristic equation given above for Case III predicts the vanishing of the volume at a finite pressure.

Something similar to the action of the model must take place in a liquid. At any instant there are collisions taking place, some free collisions similar to those of Case I, some collisions with interference like Case III, and some contacts between molecules like Case II, which are not properly called collisions at all. The momentum computation of pressure applies only to Case I. At low pressures, by far the greater number of collisions is of type I, but as the volume decreases and pressure increases, collisions of type II and III become increasingly predominant, until at infinite pressure we may suppose type II only to be present. Under these conditions, the momentum effect has absolutely no connection with pressure.

The ordinary conception of internal pressure must obviously be modified in a similar way. There are many different meanings attached to "internal pressure." One way of defining internal pressure is by constructing an imaginary surface in the interior of a liquid, and finding the momentum of all the molecules which cross this surface in unit time. This process evidently fails to have physical meaning when there are molecules in the liquid in contact with each other for any length of time. The modification of the definition necessary to meet these new conditions would be very complicated. It seems better under the circumstances to give up this conception of internal pressure altogether. Other conceptions may still be useful at high pressures; such, for example, as to regard the internal pressure as the external pressure plus the unbalanced attractive effect of the molecules at the surface of the liquid. But it is a difficult matter to define internal pressure in such a way as to have a physical meaning for one of Maxwell's demons inhabiting the interior of a liquid.

Accordingly, in the previous discussion no use has been made of this "internal pressure."

The usual kinetic conception of temperature must undergo modification at high pressures just as our kinetic conceptions of pressure. We think of the temperature of a gas as proportional to the average kinetic energy of translation of its molecules, the translational energy being the energy of the center of mass during free flight. Now it is inconceivable that at infinite pressure there should be any free flight, that is, there can be no kinetic energy of the molecule as a whole, but it is also inconceivable that at infinite pressures a substance should not possess temperature and be capable of temperature equilibrium with surrounding objects. Our model of the molecule may be helpful to us again. When the volume decreases beyond a certain limit, we saw that the boundaries of the molecule become fixed in position, and that the temperature is represented by the energy of internal agitation. This suggests that temperature changes in character from an affair of the molecule as a whole at low pressures to an affair of agitation within the molecule at high pressures. The behavior of the specific heats of gases and solids also strongly suggests the same thing. We compute the specific heat at constant volume of a gas by supposing that the kinetic energy of translation of each molecule must be increased by a fixed amount to produce a rise of temperature of one degree. But for most solid elements the law of Dulong and Petit holds, which is equivalent to the statement that to increase the temperature of a solid by one degree we must increase the energy of each atom by a fixed amount. Now a microscopic analysis of a solid like iron discloses a crystalline structure of great complexity; we find it hard to think that there are not groups of associated molecules and that the molecules are monatomic. It appears, then, that temperature has become connected somehow with what is going on in the atom. It view of this it would seem that another conception of temperature is desirable. It must be such a conception as not to be at variance with what we suppose to happen in a gas or a solid.

The material for such a conception is at land. It is a property common to the temperature energy of a gas molecule and to the internal energy of our suppositious molecule, that it is constantly in a state of flux, changing during collision from kinetic to potential and back to kinetic again. A natural generalization, then, is as follows: Temperature is proportional to that part of the energy associ-

ated with a representative molecule which undergoes periodic changes from kinetic to potential and back to kinetic. In complicated cases where the transformation from kinetic to potential does not take place simultaneously in all parts of the atom, an equivalent generalization is: Temperature is the difference between the maximum and minimum potential energy of a representative molecule. This evidently applies to both the extreme cases above; the one for which temperature is proportional to kinetic translational energy, and the one for which it is proportional to internal energy. In one respect these two extreme cases are not entirely unlike; in accordance with the law of equipartition, only a certain proportion of the total energy communicated to a molecule of a gas becomes kinetic; the rest goes to the internal degrees of freedom. So that an increase of temperature always carried with it an increase of the internal energy of the molecule. Whether this internal energy also oscillates in character between kinetic and potential is not obvious.

Of course the justification of this proposed general definition of temperature must be furnished by experiment. It does have the advantage, however, of being applicable at high pressures where the ordinary definition breaks down completely, and it does agree with our physical feeling of what temperature must be in the case of one very simple model of a substance under high pressure.

The effect of this conception of temperature on our conception of the equipartition of energy between the different degrees of freedom is interesting. At high pressures, where the molecules press on each other from all sides, one degree of freedom has been lost (or more properly three) namely, the possibility of motion of the molecule as a whole. We may suppose, if we like, that under these circumstances the total energy is equally divided between the remaining degrees of freedom. Now at any instant in a liquid, there are molecules with varying degrees of freedom, according to the kind of collision in which they are entangled. Furthermore, the same molecule at different stages of its career may enjoy a different number of degrees of freedom. When the degrees of freedom change, there must follow a redistribution of the total energy among the remaining degrees of freedom, and this process takes time. The result is that we cannot ascribe to the average molecule of the substance any definite number of degrees of freedom. The number cannot be an integer in the first place, and in the second place must vary continuously as pressure varies.

The idea that the temperature of a substance need not be propor-

tional to the kinetic energy of translation of the molecules is not new. For instance, there is a recent paper by Brillouin,[59] in which he discusses at length the possible necessity of a change in the usual definition of temperature as the volume changes.

One other very important consideration which we shall probably be obliged to introduce into a theory valid for high pressures has already been mentioned several times in the discussion of the various thermodynamic properties. It is this; in gases we think of the molecules as perfect spheres, but at high pressures we shall undoubtedly have to recognize that they possess more complicated shapes. It is inconceivable that a molecule should not have a characteristic shape; we cannot well imagine the possibility of so fitting together the atoms of a complicated organic compound as not to produce some irregularities in the molecule. Shape becomes increasingly important at high pressures where the molecules are forced together and constrained to adapt themselves as best they can to each others irregularities. Beside the possibility of shape, there is the possibility that there are local centers of force in the molecule; that we cannot regard the molecule as a homogeneous sphere exerting a force towards its own center, but that when we approach too close to the molecule, there are individualized centers of force that begin to act of their own account. This again, seems by no means a forced conception.

Along with the idea of molecules with shape goes the conception that at high pressures these shapes must be forced to more or less adapt themselves to each other; in other words, the molecules must begin to show traces of regular arrangement. The regularity is by no means the thorough going regularity of a crystal in which the molecules are permanently moored to certain mean positions: the molecules of the liquid still circulate about among each other, but as they slide past each other there may be a growing tendency at higher pressures to point the long axes in the direction of relative motion, for example. Just as at a crowded ball room, there is a tendency for the throng of young men making their way to and from the refreshment room to hold their plates out from them in the direction of motion. This increasing order of arrangement seems not only natural, but inevitable at high pressures. It may ultimately terminate in crystallization. We should expect furthermore, at equal volumes, there should be nearer approach to order at lower temperatures where the violence of temperature agitation is less.

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59 Brillouin, Ann. Chim. et phys., **18**, 387–400 (1909).

Now the combination of these two effects, namely that when the molecules come very close to each other the attractive forces depend on the orientation as well as on the mean distance apart, and that the molecules may assume a greater uniformity of arrangement, has far reaching consequences that provide the possible explanation of all the complicated effects which we have found to exist. Thus, if we consider two possible configurations of the liquid, each having the same volume, but one with a more orderly arrangement of the molecules, we see that the more orderly arrangement involves a greater effective space open to occupation. One consequence is that the more orderly arrangement has the greater compressibility. One striking example of this has been found in the case of mercury. The compressibility of solid mercury has been found to be less than the compressibility which the liquid would have at the same temperature if it could be compressed without freezing to the same volume as the solid.

In the detailed discussion of the thermodynamic properties it has been shown that we have here a possible explanation of many complicated effects. It explains increasing compressibility with rising pressure, decreasing compressibility with rising temperature, increasing thermal expansion with increasing pressure, and decreasing expansion with rising temperature. It is not necessary to go into the details of the argument again. It is to be emphasized, however, that we have here a mechanism capable of explaining a bewildering array of experimental facts. There must be at least some validity in the point of view.

Not much has been said in the explanation above of the results of possible association, because under high pressures, when the molecules find difficulty in adapting themselves to the space at their disposal, it seems unlikely for groups of molecules to unite themselves into very close knit units. The molecules, on the other hand, do apparently preserve their individuality under these high pressures, and do not break up into simpler compounds. It might be expected, for instance, that pressure would transform ether into isobutyl alcohol, a substance of the same atomic constitution, but with a smaller volume. Such was not the case, however. But it may be that association does play an important part at low pressures. In this case it would be capable of explaining various irregularities in very much the same way as suggested above. For instance, if association takes place with decrease of volume, the thermal expansion or compressibility may be

greater at lower than at high temperatures. Association has been discussed in greater detail on page 104.

The results have exhibited one striking feature which has been frequently emphasized, namely that at high pressures all twelve liquids become more nearly like each other. This suggests that it might be useful in developing a theory of liquids to arbitrarily construct a "perfect liquid" and to discuss its properties. Certainly the conception of a "perfect gas" has been of great service in the kinetic theory of gases; and the reason is that all actual gases approximate closely to the "perfect gas." In the same way, at high pressures all liquids approximate to one and the same thing, which may be called by analogy the "perfect liquid." It seems to offer at least a promising line of attack to discuss the properties of this "perfect liquid," and then to invent the simplest possible mechanism to explain them.

Summary of Results.

These measurements have disclosed an unexpectedly complicated state of affairs at high pressures, in many respects the exact opposite of what we would expect from the behavior at low pressures. The compressibility may decrease with increasing temperature, or in a few cases may increase with increasing pressure. The thermal expansion also may decrease with increasing temperature or increase with increasing pressure. The peculiarity of thermal expansion with respect to temperature is possessed by all liquids above 3000 kgm. This has been shown to have a bearing on previous theories. Of the other thermodynamic properties, perhaps the most important is the internal energy. This passes through a minimum and then increases again with increasing pressure. The reason is that beyond a certain pressure the attractive forces do less work than is done by the external forces in compressing the molecule.

Among considerations which would seem to be of importance for a theory of liquids at high pressures, that of the shape of the molecules is worthy of attention. It is inconceivable that the molecules should not have shape, and it is natural to suppose that the shape will play an important part when the molecules are forced into close contact. It is shown in detail that considerations of this sort offer possible explanations of the complicated effects actually found. Other modifications of the ordinary conceptions of liquids that may be necessary have to do with our ideas of the kinetic origin of pres-

sure and temperature. There can be no doubt that at high pressures there are other than kinetic effects involved at least in pressure.

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CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY.

THE MAXIMUM VALUE OF THE MAGNETIZATION IN IRON.

By B. Osgood Peirce.

With Three Plates.

THE MAXIMUM VALUE OF THE MAGNETIZATION IN IRON.

By B. Osgood Peirce.

Presented February, 12, 1913. Received May 3, 1913.

The first experiments on the magnetic behavior of soft iron under high excitations were made, more than sixty years ago, upon comparatively short, stout rods, so that the results were affected by the demagnetizing action of the ends of the specimen, but, even under these circumstances, several different observers [1] were able to show that if the magnetizing force to which a piece of iron is exposed be made stronger and stronger, the intensity of the resulting magnetization of the metal usually approaches a definite limit, and that this limit is practically reached in fields of such strength as are frequently used in the laboratory.

The work of Stoletow and Rowland in the early seventies of the last century, upon iron rings or toroids, made the true meanings of H, B, and I in the iron clearer, and since that time many persons [2] have attempted to determine the limiting value (I_∞), of I, as H is made to increase indefinitely. I_∞ is now sometimes called the *specific magnetism* of the material.

From some of his early work, to which he applied a peculiar method of extrapolation, Rowland inferred that in the case of soft iron, I_∞ must be about 1390, whereas Fromme obtained the value 1510 in

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1 Joule, Phil. Mag., **2**, 1839; Mueller, Pogg. Ann. **79**, 1850; **82**, 1851; Koosen, Pogg. Ann. **85**, 1852; Dub, Pogg. Ann. **90**, 1853; G. Wiedemann, Pogg. Ann. **100**, 1851; **106**, 1859; **117**, 1862.

2 Rowland, Phil. Mag. **46**, 1873; **48**, 1874; Stefan, Wiener Berichte, 1874; **97**, 1888. Wied. Ann. **38**, 1889; Fromme, Wied. Ann. **13**, 1881; Ewing and Low, B. A. A. S. Report 1887; Phil. Trans. **180**, 1889; H. E. J. G. duBois, Phil. Mag. **29**, 1890; Roessler, Elektrotechnische Zeitschrift, **14**, 1893; Jones, Wied. Ann. **54**, 1895; **57**, 1896; Gumlich, Elektrotechnische' Zeitschrift, **30**, 1909; Peirce, These Proceedings, **44**, 1908; Am. Journal of Science, **28**, 1909; Weiss, Journal de Physique, May, 1910; Hadfield and Hopkinson, Jour. Inst. Elect. Eng., **46**, 1911.

1873, and Stefan, 1400, in the following year. In 1881, however, Fromme got the value 1737 for one specimen, and in 1884, Weber, exposing a long rod in a solenoid to a field which had an intensity of only 900 gausses before the iron was introduced, found the corresponding value of I to be 1700.

In 1887, Messrs. Ewing and Low introduced a new and most ingenious method for experimenting upon slender isthmuses of iron and steel under very high excitations and showed that different specimens of soft iron often behaved very differently in very strong fields. For one brand of fine Swedish iron, they found the final value of I to be only 1620, while for a certain kind of Bessemer steel, the value I_∞ was as high as 1770.

Du Bois published in 1890 the results of a series of experiments upon iron in very intense fields the strengths of which he had determined by optical means. In order to obtain, for each brand of material, the Kerr's constant which he needed, he first examined an ellipsoidal test piece of the material in much weaker fields, in a solenoid. In a typical case, the soft iron ellipsoid of revolution was 18 centimeters long and 6 millimeters in diameter at the centre. The solenoid was 30 centimeters long and consisted of 1080 turns of insulated wire wound in twelve layers of about 4 centimeters mean radius. The field intensity at a point 9 centimeters from the centre of the solenoid was about 6% less than at the centre and this introduced a correction into the formula for I. The moment acquired by the bar when it was under excitation was determined, after the effect of the current in the solenoid had been compensated for, by the indications of a magnetometer in Gauss's A Position with respect to the specimen. The correction for the ends of the ellipsoid was made by the use of the formula $H' = H - 0.052\ I$. We shall find it convenient to refer to these results later on in this paper and some of them appear in Table I.

TABLE I.

H'.	I.	H'.	I.
100	1410	600	1680
200	1522	800	1695
300	1590	1000	1703
400	1630	1300	1712
500	1661		

In the stronger fields the results were not so regular, for the specimen was magnetized between the poles of a powerful electromagnet

and the fields were far from uniform. The final value of I which du Bois obtained lay somewhere between 1700 and 1750.

A paper by Roessler in the Elektrotechnische Zeitschrift for 1893 describes some experiments very like those made by du Bois with the solenoid mentioned above. Roessler's solenoid was 1 meter long and consisted of 16 layers of wire 3 millimeters in diameter. The mean radius of the solenoid was about 5.5 centimeters and the field at a point on the axis 25 centimeters from the centre was about 1% less than at the centre itself. The test piece was an ellipsoid 50 centimeters long and 1 centimeter in diameter. The results which Roessler obtained for a certain specimen of so called "soft iron" are given in Table II.

TABLE II.

H'.	I.	H'.	I.
414	1645	848	1679
481	1663	919	1681
516	1670	991	1681
587	1675	1062	1685
741	1679	1276	1683
777	1681	1312	1687

The values of I_∞ published in 1896 by E. T. Jones, who magnetized a short, slender wire of the material to be tested between the conical pole pieces of an electromagnet of the du Bois form, ranged as high as 1818; and the results of the joint work of du Bois and Jones, printed in 1899, gave values of I_∞ between 1780 and 1850.

Weiss, in 1907 and 1909, experimented upon small ellipsoids of revolution made of iron, nickel, and cobalt, placed symmetrically between the flat pole pieces of a powerful electromagnet. Each ellipsoid was about 9 millimeters long and 3.5 millimeters in diameter. The gap between the pole pieces was about 6 centimeters long and the diameter of the magnet core was 15 centimeters. An excitation of 94000 ampere turns corresponded to a field of about 9000 gausses in the gap centre. The small ellipsoid was suddenly drawn out of the field through a hole in the axis of one of the pole pieces and the flux change in a test solenoid outside the iron was determined. Weiss's values of I_∞ were 1731 and 1706.

Gumlich in 1909 made a series of extremely accurate determinations of the final value of I in soft iron by the Isthmus Method, using an electromagnet of the du Bois form, which was furnished with two soft pole pieces fastened together with the isthmus between them and

capable of being rotated together about a horizontal axis perpendicular to the pole axis, so as to reverse suddenly the sign of the magnetization in the test piece. Each specimen was 28 millimeters long and 3 millimeters in diameter. To make sure that the lines of induction in the test piece were throughout parallel to each other, Gumlich sometimes used soft iron rings slipped over the specimen. Gumlich's value of I_∞ was 1725.

In December, 1910, Messrs. Hadfield and Hopkinson printed the results of a very carefully carried out and very elaborate investigation into the question whether in such combinations of iron and less magnetic substances as are in practical use, the specific magnetism of any piece of the material multiplied by the mass of the piece is simply equal to the sum of the products obtained by multiplying the mass of each constituent in the specimen by its specific magnetism. They came to the conclusion that although this rule seems not to hold in certain alloys of iron, nickel, and manganese, it is really fulfilled in many practical cases.

They used a modification of the Isthmus Method very skilfully, employing an electro-magnet like, if not identical with, the magnet which Ewing and Low had, and which was made for the first isthmus experiments, under the direction of W. Low, Esquire, of Balmakewan.

Hadfield and Hopkinson had at command a large number of alloys specially made at the Hecla Works, for research purposes, and the analyses of their test pieces are therefore beyond question. They found that in their annealed iron-carbon steel, where other elements were nearly absent, the specific magnetism was less than for their standard iron by a percentage equal to about six times the percentage of carbon. In such a case they assumed that there are two constituents, pure iron, and iron carbide (Fe_3C) in mechanical mixture, the percentage of the carbide present being 15.5 times that of the carbon in the steel. The "pure iron" used as a standard was a sample of Swedish iron (Maker's mark "S. C. I.") containing less than 0.2 per cent of impurities. Of this they used two specimens: one was 6.26 mm. long, and 3.18 mm. in diameter and weighed 0.385 grammes; the other was 15.92 mm. long and 3.19 mm. in diameter, and its weight was 0.99 grammes. Both yielded the same value (1680) for the specific magnetism. Table III, obtained from measurements of one of the curves given by Hadfield and Hopkinson, reproduces their results sufficiently well. Most of their pieces of steel were slightly less dense than the S. C. I. iron and their final values of I_∞ give the magnetization vector per unit volume of matter of the same density as the iron.

It is now possible to get in the market large pieces of iron which has less than 0.03% of impurities all told, and I have used Norway iron

TABLE III.

HADFIELD AND HOPKINSON'S VALUES OF THE SPECIFIC MAGNETISM OF IRON AND CARBON ALLOYS.

Percentage of Carbon.	Specific Magnetism.
*	1680
0.5	1630
1.0	1580
1.5	1530
2.0	1480
2.5	1430
3.0	1380
3.5	1330

99.87% pure, as well as many other specimens of nearly this excellence. In some cases the specific magnetism seemed to be about 1740 and in others less than 1700. For these determinations I have usually employed some form of isthmus method.

TABLE IV.

SATURATION VALUES OF THE MAGNETIZATION VECTOR IN IRON.

Rowland,	(1873–8)		1390
Stefan	(1874)		1400
Fromme	(1873)		1510
Fromme	(1881)		1737
Weber	(1884)	(H = 900)	1700
Ewing and Low	(1887–9)	1620 to	1740
DuBois	(1890)	(H = 1200)	1710
Roessler	(1893)	(H = 1276)	1688
Jones	(1896)		1818
DuBois and Jones	(1899)	1780 to	1850
Weiss	(1907)		1731
Gumlich	(1909)		1725
Peirce	(1909)	1738 to	1751
Weiss	(1910)		1706
Hadfield and Hopkinson	(1911)		1680

If the lines of magnetic induction in a slender homogeneous cylinder, made of perfectly soft iron, are known to be straight and parallel to the generating lines of the cylinder, we may infer that the induction vector — which in this case must be solenoidal and lamellar in the metal,— has the same intensity throughout the space considered. If, moreover, the lines of force in the air about the cylinder and near it on all sides, seem to be straight, we may believe, since the tangential components of the magnetic force and the normal component of the induction are continuous at the surface of the iron, that the lines of force and induction in the metal are straight and parallel to the lines of the cylinder and to the lines just outside the metal in the air. If, therefore, by means of a test coil of very fine insulated wire wound tightly around the cylinder, and a somewhat larger coaxial coil which does not extend into any portion of the air where the lines of force are not straight, we determine B in the metal and H in the closely surrounding space, the ratio of the two may be supposed to give the value of the permeability in the iron. This is the theory that underlies one form of the "Isthmus Method" of measuring the value of the magnetization vector in the metal at high excitations. If the results are to be satisfactory, great care must be taken to make sure that the magnetic lines just outside the isthmus are really straight in the region to be used, and the dimensions of the test coils must be determined with the aid of trustworthy comparators with great accuracy. The larger test coil must be mounted upon some sort of support, if it is to keep its form unchanged, and the choice of material for a spool is very narrow. No brass or copper that I have ever tried is unmagnetic in very strong fields; paraffine wax and ebonite are often paramagnetic and introduce errors into the readings. Silk insulation for the wire of which the test coils are made is inadmissible without careful examination and even shellack, when dried from an alcoholic solution, is almost always strongly magnetic.

The form of bobbin used by Ewing and Low requires a fresh outer test coil for each specimen, but the little rods inserted at the ends into holes in the pole pieces, as in the work of Gumlich, or the shorter rods butted against the faces of the pole pieces, as in the work of Hadfield and Hopkinson, do not have this disadvantage.

If the lines of force in the air about the isthmus are practically straight for one excitation they often cease to be so when the intensity of the field is much increased. If, with soft iron pole pieces the lines are parallel for a soft iron bobbin, they may not be even approximately so for a bobbin of fairly hard steel, as I have found to my cost in a somewhat large experience.

These and other difficulties lie in the way of anyone who attempts to use the Isthmus Method in its original form, and every modification of it, whatever advantages it has, usually introduces some new problems. Notwithstanding all this, the method is a most useful one and has a much wider application than has usually been given it. No other way that has been proposed of making magnetic measurements at very high excitations is nearly so good, and the test pieces now employed are small and convenient to make.

There is still in many cases some uncertainty in the determinaton of H, and Hadfield and Hopkinson discuss the subject in trying to account for the differences between their results[3] and those of Gumlich, obtained at the Reichsanstalt. Moreover, there is sometimes irregularity in the values of I measured by the Isthmus Method[4] for a single specimen. For these reasons, it has seemed to me worth while to push the use of the solenoid for magnetizing test pieces farther than has yet been done, to make sure that there are specimens of metal in which I is higher than 1700 even in much weaker fields than those which the Isthmus Method furnishes. This is especially desirable if we wish to be able to determine the constitution of a large mass of steel by a quick measurement of the specific magnetism of a small test piece in an electromagnet arranged for the purpose, as has been proposed.

According to the molecular theory of magnetization of Weber and Ewing, the molecules, which lie with their magnetic axes in all directions when the metal is in the neutral state, tend to turn in the direction of any magnetic field to which the iron may be exposed, though they are hindered from doing so by the interaction of the molecules themselves. When, however, the applied field is made strong enough to overcome these intermolecular forces, in large measure, all the axes of the elementary magnets point practically in the same direction. It is evident, therefore, that unless the applied field affects the moments of the elementary magnets of which the metal is made up, the magnetic moment (I) of the metal per unit volume should remain nearly constant after the excitation has gone beyond a certain large value. This maximum magnetization is very different in different metals and we may well consider it as characteristic of a material.

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3 Journal of the Institution of Electrical Engineers, Dec., 1910, p. 253.
4 Ewing's Magnetic Induction in Iron and Other Metals, Tables XI, XII.

Apparatus and Method of Procedure.

Figure 1 shows diagrammatically the general arrangement of the great array of apparatus used in making the measurements described in this paper. This apparatus was adjusted and some of it constructed

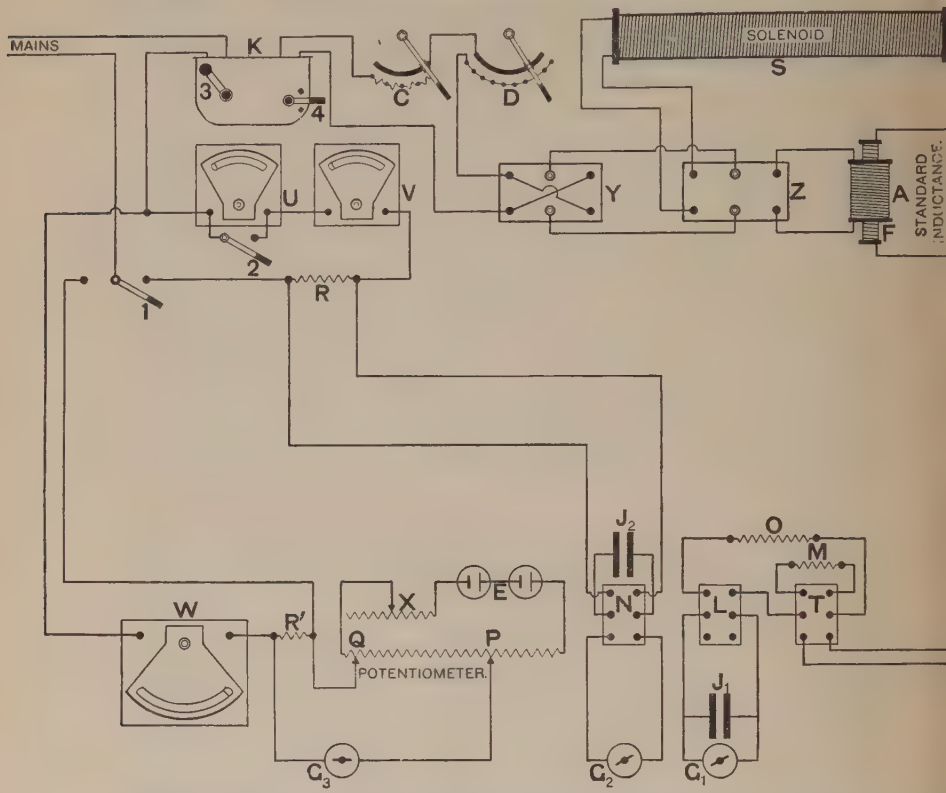

Figure 1. This Figure shows diagrammatically the general arrangement of some of the apparatus used in making the observations described in this paper. The elaborate devices for demagnetizing the specimens are omitted for simplicity.

by Mr. John Coulson of the scientific staff of the Jefferson Laboratory, who has worked with me at every stage of the investigation, and to whose skill and patience I am deeply indebted. Many details are omitted from the figure. The devices for demagnetizing the specimens to be tested will be described later on.

It is evident that in such measurements of magnetic flux changes as are necessary in the work described in this paper, it is of fundamental importance that the ballistic galvanometers used be correctly calibrated, and we used a number of standards of mutual inductance, most of them rather larger than those commonly employed for such purposes,

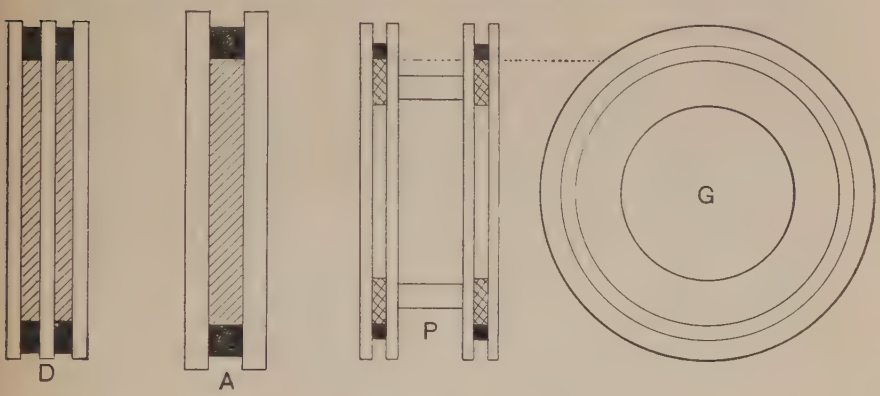

FIGURE 2. Three standards of mutual inductance.

since our rather slowly moving galvanometer was not very sensitive. We had in all seventeen mutual inductances for our calibrations. Of these five have been measured for us this year at the United States Bureau of Standards, and seven others are of such forms that their values may be calculated by well known methods. We found one of Doctor Campbell's Variable Standards of Mutual Inductance (which was very kindly lent to us by Professor Kennelly), most useful. It proved to be very accurately calibrated, and it agreed closely at all points with the standards determined for us at Washington.

An elaborate series of comparisons of our inductances occupied Mr. Coulson and myself for more than two months, because we found that three or four of those which, according to our computations based upon their geometrical forms, should have certain values, seemed to have slightly different values, though they did not seem to be quite constant. This phenomenon puzzled us at first and gave us much trouble, but we believe, after all our work, that the ebonite used as a core in three of them is very slightly susceptible in a strong magnetic field, that the split thick brass tube used as a core for one of our solenoids is sufficiently paramagnetic to affect the field inside it perceptibly, though another solenoid constructed in a similar manner seems

free from this difficulty, and finally, that the white silk triple covering of some of our wire is hygroscopic and that when a closely wound coil of it is damp, there may be a very little leakage from turn to turn through the insulation, under very strong excitation. In any event, we have eliminated all error from these sources, and we believe that the inductances of the standards we have finally used may be depended upon to at least the twentieth of one per cent.

The shapes of three of our standards are shown in Figure 2. In D, the three larger plates (and the shaded cores) are of plate glass about 29 centimeters in diameter. The cores were mounted by Mr. Thompson in an engine lathe, and were ground for about two days, under a constant flow of soda water, by a rapidly turning carborundum wheel fastened to the tool post and driven by its own motor, while the lathe moved slowly. In this way the plates were made very accurately circular. A is also wound upon a plate glass spool, but the two coils are wound together from two spools of wire triply covered with white silk. P consists of two spools with plate glass ends, but the shaded cores are ebonite rings. G shows a side view of P.

The magnetizing solenoid consists of about 300 kilograms of triply covered Number 10 copper wire wound uniformly with great care, by Mr. George W. Thompson, upon a massive brass spool 186.2 centimeters long in inside measurement. The inner coil has 8117 turns in 14 layers, and a resistance at room temperatures of about 7.7 ohms. The outer coil, of slightly different wire, has 5872 turns in 10 layers, and a resistance of about 9.8 ohms. The field intensity at different points of the axis was found for a given current in each layer separately, and it appeared from combining the results, that a current of one ampere sent through the whole inner coil gives rise to a field of intensity 54.71(3) gausses at the centre and 54.60(5) gausses at a point 50 centimeters from the centre, on the axis. A current of one ampere sent through both coils in series creates an electromagnetic field of intensity 94.19(5) gausses at the centre and 93.77(5) gausses at a point 50 centimeters from the centre, a difference of nearly one half percent. The outside diameter of the solenoid is a little less than 20 centimeters.

For currents up to 31.5 amperes, corresponding to a field of about 2900 gausses, the coils were used in series attached to the 550 volt circuit of the Harvard University plant. For stronger fields of 5000 gausses or more, the coils could be attached in parallel to this circuit

with a standard amperemeter in each branch. For the preliminary experiments, fields stronger than 4600 gausses were not needed.

The thick, solid-drawn brass tube upon which the wire was wound carried a stream of tap water to keep the specimen at a constant temperature. The test coil was wound upon the test piece after the latter had received a very thin film of varnish. The test coil, after it had been made, was varnished and the whole was then placed for about half an hour in a stream of hot air to harden the coating. The leads were enclosed in a very thin tube of rubber, the test coil was covered with a rubber shield, and melted paraffine wax was then run into the ends of this shield so as to keep the test coil absolutely dry. In this manner all leakage from turn to turn of the triply silk covered wire of which the test coil was made was avoided. In many cases two test coils were wound side by side upon each specimen, but the results, after we had learned how to make the coils properly, were so nearly identical for both coils that we sometimes used only one. In all cases the differences, if there ever were any real differences, were far smaller than the unavoidable errors of ballistic galvanometer reading.

The reversal of a strong current in the circuit of a solenoid with so great an inductance as this one, has to be managed carefully. The main reversing switch, when it was slightly pulled, automatically put the solenoid in parallel with a noninductively wound resistance higher than its own, and, after the handle was raised higher, broke the main circuit so that the discharge from the solenoid could pass through the auxiliary resistance. The process was inverted when the switch handle was pushed down. This switch (Figure 3, Plate 1) was designed and made by Mr. Coulson.

To prove that the field in the solenoid, when a given current passes through the circuit, is really what it should be, according to the calculation, a very carefully made test coil without iron was placed in series with the secondary of a standard of mutual inductance and the field was thus measured. By this means it was shown that there was no appreciable leakage between the turns of the solenoid — a very common fault of the exciting coils of electromagnets — and that there was not enough iron in the brass of the reel to affect the field strength sensibly. So far as we can determine the fact by our many and repeated tests, the solenoid has not been injured by use and is very perfect. It is firmly mounted on a solid oak frame so that its axis is horizontal and perpendicular to the meridian.

The dimensions of the iron test pieces and of the standard induc-

tances were obtained with the help of a set of micrometer screw gauges by Brown and Sharpe. The smallest one of these was used for determining the diameters of the specimens and of the coils wound upon them. The accuracy of this gauge was tested by a comparator (which had a screw by Gaertner), and by another comparator (by Zeiss) which reads directly to microns.

An illustration, the case of a specimen of American Ingot Iron, will show how much error would be introduced into the value of the specific magnetism of the iron by a given error in measurement of its dimensions. The length was 100 cm., the diameter of the bare iron, 1.278(5) cm. and the mean diameter of the test coil, 1.326 cm. The coil consisted of 100 turns of copper wire triply covered with white silk, and as the dimensions show, the flux through it was $128.32\ B + 9.8\ H$. The last term which shows the correction for the air flux linked with the coil, is relatively small at feeble excitations, and even when H rises to 2800 and B becomes about 24500, the whole term is less than 1% of the flux through the iron. Moreover the value of the term may be found to within one twenty-fifth of its value without trouble. An error of 0.001 in measuring the diameter of the iron might make an error of three units in the last place in the value of the specific magnetism and this makes it desirable to use exactly round rods. The piece here described was cut out of a large bar with great skill, at the works of Messrs. Barbour and Stockwell.

At high excitations, the corrections for the effect of the ends of the cylindrical test pieces are, of course, much less than those which according to theory and to the formulas of DuBois and of Shuddemagen are necessary in low fields. I shall hope to discuss this matter at length in another paper, and need only state here that the correction for a piece of the dimensions used was practically negligible in fields of strength above 2000 gausses.

The rods to be annealed were first packed tightly in fine iron filings in a piece of pipe the ends of which were closed by screw caps, and the whole was carefully supported perpendicular to the meridian in a special gas heater where it would be exposed to several hundred flames driven by a power compressor. In this manner a piece 150 centimeters long could be heated very uniformly. After the specimen had been kept for perhaps an hour at a temperature considerably above the critical point of the iron it could be then allowed to cool very slowly *in situ*, protected from magnetic action.

If a slender rod of iron be placed inside a long solenoid which is in the secondary circuit of a powerful open-core transformer, and if

while the primary circuit is attached to the alternate current mains, the secondary coil of the transformer be slowly drawn off the core and the primary coil, by help of some mechanical device, it is possible to send through the solenoid a long series of currents alternating in direction and gradually decreasing in intensity and thus to demagnetize the iron rod very well. We had an apparatus of this kind permanently connected with our apparatus, but it was not shown in Figure 1 lest the diagram be too complex.

When the direction of a strong electrical current in the circuit of the large solenoid (S) in which the iron rods to be tested were magnetized, was suddenly reversed, some time was needed to establish the new current in its full value, and the change in the magnetic flux through the test coils wound upon the rods was not complete until after several seconds. This fact, due to the large inductance in the circuit, made it unsafe to employ a ballistic galvanometer of ordinary type for measuring this flux change, and we had recourse to a long period instrument of a kind which has been used for a number of years in the Jefferson Laboratory. The particular galvanometer (G) we chose, had a period of 156 seconds which was quite long enough for our purposes, but we had a much more slowly moving instrument at hand in case of need. Any fairly long throw of G could be determined with an error of less than one tenth of one per cent, and we could do better than this by careful repetition. G is shown in Figure 4, Plate 1.

The main currents in the solenoid circuit were measured with the help of a series of Weston Amperemeters (two of which are shown diagrammatically as U and V in Figure 1) properly arranged for the special intensity ranges we needed, but the accurate determination of large currents was made by aid of a potentiometer (Figure 5) with standard cadmium cells, which measured the potential drop across a standard one hundredth of an ohm resistance (R) by Crompton, which had been tested against another standard by Wolff. The largest currents we used could not very well be allowed to run very long through the coils because the amount of heat set free in the circuit was enormous. Indeed, with an energy expenditure of more than fifty kilowatts, the heating problem, in spite of running water in the core of the solenoid needed careful consideration. As a matter of fact, the only difficulty we finally encountered was a slight falling off of our largest currents with repeated throws, owing to a little increase in the resistance of the circuit, and this came at a place where the flow of inductance through the test coil changed very slowly with H. To save time we arranged a standard condenser (Elliot Brothers,

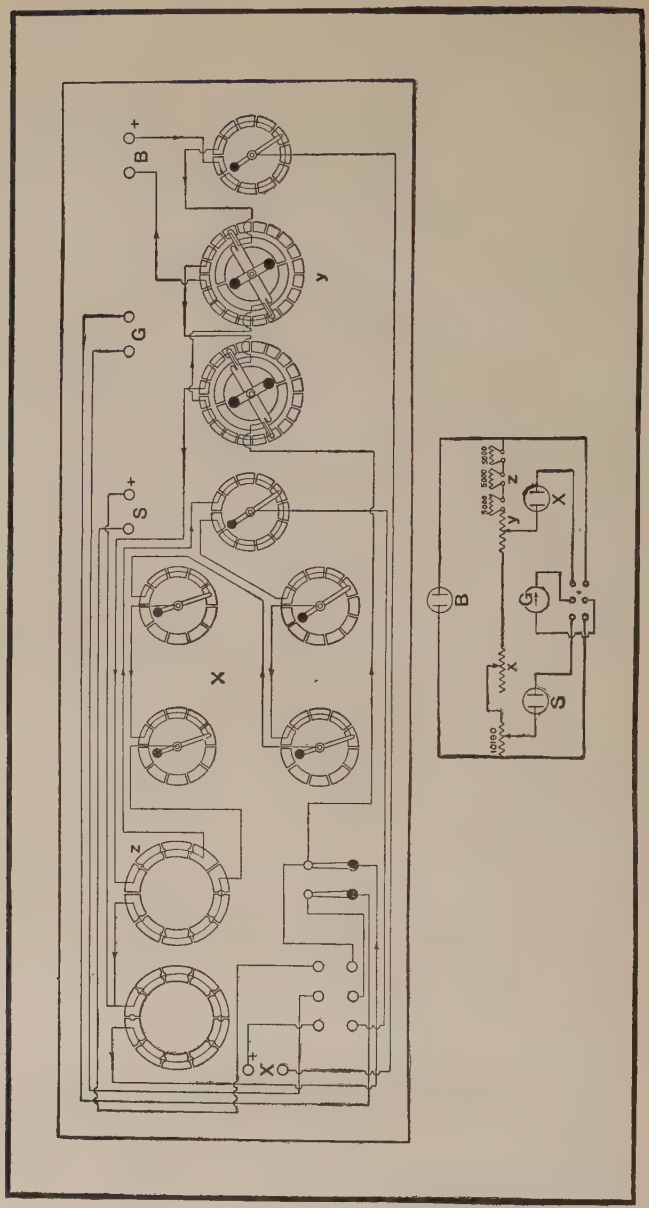

FIGURE 5. The standard potentiometer.

No. 72) so that it became automatically charged at the terminals of R just as the main switch was reversed, and the charge could then be measured at our ease four or five seconds after the switch had been thrown over. By these means we avoided the delay which would have resulted if we had been obliged to read the amperemeters before the reversal.

Besides this slowly moving ballistic galvanometer, we used three other mirror galvanometers, one for the condenser throws, one for the potentiometer, and one for the accurate comparison of our inductances, and in addition, a large standard laboratory amperemeter (W), by Weston, which could be checked at any instant against the potentiometer. This beautiful instrument has an engine divided scale 31 cms. long.

At very high excitations, the reversal of any switch of ordinary construction gives rise to a very unpleasant explosion, and we often made use of a large controller (K) constructed by the General Electric Company for use upon electric cars. This was very kindly lent to us by Mr. F. W. Lieberknecht, and served an excellent purpose. We do not need to describe a large number of auxiliary amperemeters and galvanometers used in our work.

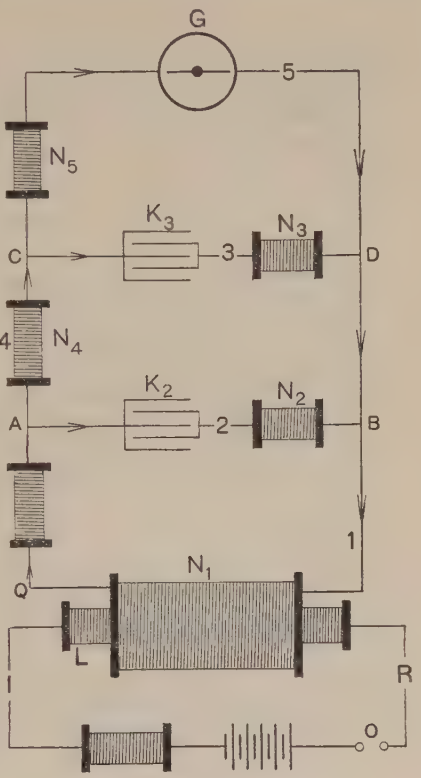

FIGURE 6.

THE USE OF CONDENSERS IN THE INDUCTIVE SECONDARY CIRCUIT.

The inductance in the secondary circuit, which contained the test coil or coils, the secondary coils of the inductance standards, and the

coil of the large ballistic galvanometer, was usually considerable and the strain upon the insulation of the wire was sometimes large when a powerful current in the primary circuit was suddenly reversed. Occasionally, there seemed to be some leakage in this circuit, so we introduced a number of condensers into the circuit in the attempt to reduce

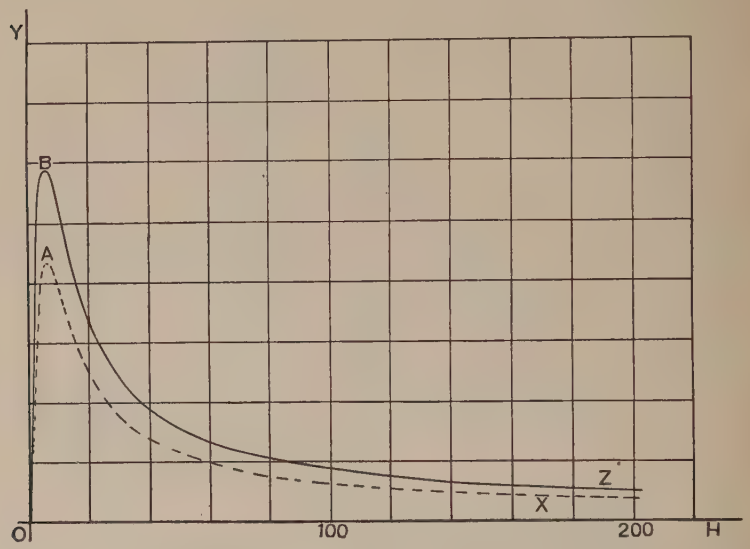

FIGURE 7. This figure shows the forms of the curves obtained by plotting the permeability and the susceptibility of a certain kind of soft iron against the exciting field. These curves, OBZ, OAX, are drawn to different scales.

the stress. What the exact effect of such condensers in a complex circuit will be when the breaking arc in the primary circuit is oscillatory, it is usually impossible to predict, because some necessary data are wanting or because the literal equations are of too high a degree to be solved, but certain general facts are clear. The following analysis treats some questions, as applied to a circuit taken for illustration, which are really, perhaps, too elementary to need any discussion.

Figure 6 represents two neighboring circuits:—

(*a*) A primary circuit of total resistance R, and total self inductance L, which contains a constant battery of voltage, V, and carries a current I. This circuit is furnished with a gap (O) which may be closed or opened at pleasure.

(*b*) A secondary circuit of several branches, which has no battery,

but which is linked with the primary circuit by the mutual inductance, M. The branch AQB or (1), which is directly coupled with the primary, has a resistance R_1, a total self inductance N_1, and carries a current I_1. The branches AB, CD, or (2), (3), contain condensers of capacities K_2 and K_3 respectively. Their resistances are R_2 and R_3, their self inductances, N_2 and N_3 and they carry currents I_2 and I_3. The branches (4) and (5) have no condensers. Their resistances are R_4 and R_5, their self inductances, N_4, N_5, and their currents, I_4 and I_5. The current in DB, which has a negligible resistance, is, of course, I_4.

If accents are used to denote differentiations with respect to the time, an easy application of Kirchhoff's Laws to these two circuits leads to the equations:—

$$
\begin{aligned}
&V - L\cdot I' - M\cdot I'_1 = R\cdot I,\\
&-M\cdot I' - N_1\cdot I_1' - N_4\cdot I_4' - N_5\cdot I_5'\\
&\qquad = R_1\cdot I_1 + R_4\cdot I_4 + R_5\cdot I_5,\\
&-M\cdot I' - N_1(I_2' + I_3' + I_5') - N_2\cdot I_2' - Q_2/K_2\\
&\qquad = R_1(I_2 + I_3 + I_5) + R_2\cdot I_2,\\
&-M\cdot I' - N_1(I_2' + I_3' + I_5') - N_4(I_3' + I_5') - N_3\cdot I_3' - Q_3/K_3\\
&\qquad = R_1(I_2 + I_3 + I_5) + R_4(I_3 + I_5) + R_3\cdot I_3,\\
&I_1 = I_2 + I_4 = I_2 + I_3 + I_5,
\end{aligned}
\tag{1}
$$

or

$$
\begin{aligned}
&(L\cdot I' + R\cdot I) + M\cdot I_2' + M\cdot I_3' + M\cdot I_5' = V,\\
&M\cdot I' + (N_1\cdot I_2' + R_1\cdot I_2) + (N_1\cdot I_3' + N_4\cdot I_3' + R_1\cdot I_3 + R_4\cdot I_3)\\
&\quad + (N_1\cdot I_5' + N_4\cdot I_5' + N_5\cdot I_5' + R_1\cdot I_5 + R_4\cdot I_5 + R_5\cdot I_5) = 0,\\
&M\cdot I'' + (N_1\cdot I_2'' + N_2\cdot I_2'' + R_1\cdot I_2' + R_2\cdot I_2' + I_2/K_2)\\
&\quad + (N_1\cdot I_3'' + R_1 I_3') + (N_1\cdot I_5'' + R_1\cdot I_5') = 0,\\
&M\cdot I'' + (N_1\cdot I_2'' + R_1\cdot I_2') + (N_1\cdot I_3'' + N_4\cdot I_3'' + N_3\cdot I_3''\\
&\quad + R_1\cdot I_3' + R_4\cdot I_3' + R_3\cdot I_3' + I_3/K_3)\\
&\quad + (N_1\cdot I_5'' + N_4\cdot I_5'' + R_1\cdot I_5' + R_4\cdot I_5') = 0.
\end{aligned}
\tag{2}
$$

If, for I we write $I_0 + V/R$, the second number of the first equation becomes zero, while all the equations remain otherwise unchanged in form, and it follows that every one of the currents satisfies a single linear differential equation of the sixth order with constant coefficients

and that if a, b, c, d, e, and h are the roots of the equation formed by equating to zero the determinant,

$$\begin{vmatrix} Lx+r & Mx & Mx & Mx \\ Mx & N_1x+R_1 & \{N_1x+N_4x+R_1 \\ & & \quad +R_4\} & \{N_1x+N_4x+N_5x \\ & & & \quad +R_1+R_4+R_5\} \\ Mx^2 & \{N_1x^2+N_2x^2+R_1x \\ & \quad +R_2x+1/K_2\} & N_1x^2+R_1x & N_1x^2+R_1 \\ Mx^2 & N_1x^2+R_1x & \{N_1x^2+N_4x^2+N_5x^2 \\ & & \quad +R_1x+R_4x+R_5x \\ & & \quad +1/K_3\} & \{N_1x^2+N_4x^2+R_1x \\ & & & \quad +R_4x\} \end{vmatrix} \quad (3)$$

then

$$\begin{aligned} I &= Ae^{at} + Be^{bt} + Ce^{ct} + De^{dt} + Ee^{et} + He^{ht} + \frac{V}{R} \\ I_2 &= \alpha_2 Ae^{at} + \beta_2 Be^{bt} + \gamma_2 Ce^{ct} + \delta_2 De^{dt} + \epsilon_2 Ee^{et} + \eta_2 He^{ht} \\ I_3 &= \alpha_3 Ae^{at} + \beta_3 Be^{bt} + \gamma_3 Ce^{ct} + \delta_3 De^{dt} + \epsilon_3 Ee^{et} + \eta_3 He^{ht} \\ I_5 &= \alpha_5 Ae^{at} + \beta_5 Be^{bt} + \gamma_5 Ce^{ct} + \delta_5 De^{dt} + \epsilon_5 Ee^{et} + \eta_5 He^{ht} \end{aligned} \quad (4)$$

If these values be substituted in one of the Kirchhoff equations above and the coefficients of the different exponential expressions separately equated to zero, it will appear that the α's, β's, γ's, δ's, ϵ's, and η's are determinate functions of the constants of the circuit and in no way dependent upon the manner in which the currents are managed.

The other six constants (A, B, C, D, E, H) have to be computed from a knowledge of the electrical conditions which determine any problem concerning these two fixed circuits.

If, for instance, there is no current in any branch of the circuits at the outset, and if the gap, O, be suddenly closed at the origin of time, the values of the constants for all positive time satisfy the equations

$$\begin{aligned} A + B + C + D + E + H &= -\frac{V}{R} \\ \alpha_2 A + \beta_2 B + \gamma_2 C + \delta_2 D + \epsilon_2 E + \epsilon_2 H &= 0 \\ \alpha_3 A + \beta_3 B + \gamma_3 C + \delta_3 D + \epsilon_3 E + \epsilon_3 H &= 0 \\ \alpha_5 A + \beta_5 B + \gamma_5 C + \delta_5 D + \epsilon_5 E + \epsilon_5 H &= 0 \end{aligned} \quad (5)$$

and, after these have been solved, it is easy to compute the whole flow of electricity through the galvanometer, for

$$\int_0^\infty I_5\, dt = -\left(\frac{\alpha_5 A}{a} + \frac{\beta_5 B}{b} + \frac{\gamma_4 C}{c} + \frac{\delta_5 D}{d} + \frac{\epsilon_5 E}{e} + \frac{\eta_5 H}{h}\right) \quad (6)$$

If, however, when the primary current has its steady value, V/R, and there are no currents in the secondary circuit, the primary resistance be instantaneously changed from R to R', at the time $t = 0$, there is no sudden change in the current in any branch, but for all subsequent time, the constants are determined by the equations:—

$$\begin{aligned} A + \quad B + \quad C + \quad D + \quad E + \quad H &= \frac{V}{R} - \frac{V}{R'} \\ \alpha_2 A + \beta_2 B + \gamma_2 C + \delta_2 D + \epsilon_2 E + \eta_2 H &= 0 \\ \alpha_3 A + \beta_3 B + \gamma_3 C + \delta_3 D + \epsilon_3 E + \eta_3 H &= 0 \\ \alpha_5 A + \beta_5 B + \gamma_5 C + \delta_5 D + \epsilon_5 E + \eta_5 H &= 0 \end{aligned} \tag{7}$$

and it is evident that every one of the quantities, A, B, C, D, E, H, I, given by (7) has a value which bears to the corresponding value given by (5) the ratio $(R - R')/R'$, and the same relation holds between the whole discharges through the galvanometer in the two cases. If the gap be instantly opened so that R' is infinite, when the current in the primary circuit is V/R and there are no secondary currents, the galvanometer throw is equal, but opposite in sign, to the throw caused by suddenly closing the gap when all the currents are zero.

The electrokinetic energy for the coupled circuits is

$$\begin{aligned} T = \tfrac{1}{2}L \cdot I^2 + M \cdot I(I_2 + I_3 + I_5) + \tfrac{1}{2}N_1(I_2 + I_3 + I_5)^2 \\ + \tfrac{1}{2}N_2 \cdot I_2^2 + \tfrac{1}{2}N_3 \cdot I_3^2 + \tfrac{1}{2}N_4(I_3 + I_5)^2 + \tfrac{1}{2}N_5 \cdot I_5, \end{aligned} \tag{8}$$

so that the electrokinetic momenta are

$$\begin{aligned} p &= L \cdot I + M(I_2 + I_3 + I_5) \\ p_2 &= M \cdot I + N_1(I_2 + I_3 + I_5) + N_2 \cdot I_2 \\ p_3 &= M \cdot I + N_1(I_2 + I_3 + I_5) + N_3 \cdot I_3 + N_4(I_3 + I_5) \\ p_5 &= M \cdot I + N_1(I_2 + I_3 + I_5) + N_4(I_3 + I_5) + N_5 I_5 \end{aligned} \tag{9}$$

If, when I has the value $I = V/R$, and there are no other currents, the gap be instantly opened, I suddenly drops to zero, and I_2, I_3, I_5, which were 0, suddenly acquire initial values which may be determined by the fact that the electrokinetic momenta, p_2, p_3, p_5, which before the change were equal to $P_0 = MV/R$, are not altered by the impulse. After the gap is opened, the currents in the branches obey the system of equations (2), but the initial values of these currents are to be found from the equations

$$\begin{aligned}(N_1 + N_2)I_2 + N_1I_3 + N_1I_5 &= P_0 \\ N_1I_2 + (N_1 + N_3 + N_4)I_3 + (N_1 + N_4)I_5 &= P_0 \\ N_1I_2 + (N_1 + N_4)I_3 + (N_1 + N_4 + N_5)I_5 &= P_0\end{aligned} \qquad (10)$$

If then Δ denote the determinant of the coefficients,

$$\Delta = N_1N_2N_3 + N_1N_3N_4 + N_1N_3N_5 + N_1N_2N_5 + N_1N_4N_5 + N_2N_3N_5 + N_2N_3N_4 + N_2N_4N_5,$$

and the values of I_2, I_3 and I_5 just after the gap is opened, are

$$(N_3N_4 + N_3N_5 + N_4N_5)P_0/\Delta,\ N_2N_5P_0/\Delta,\ \text{and}\ N_2N_3P_0/\Delta. \qquad (11)$$

The total amount of electricity carried by the currents I_2, I_3, and I_5 are 0, 0, and Ω; and to find Ω we may integrate the second equation of the system (2) with respect to the time from 0 to ∞ and use the initial values of I_2, I_3, I_5 just found. This procedure leads to the equation:

$$\Omega = \int_0^\infty I_5 \cdot dt = \frac{P_0}{R_1 + R_4 + R_5}, \qquad (12)$$

and this is evidently the same result that would have been obtained for the whole discharge through the galvanometer, if the branches (2) and (3), with their condensers, were removed from the secondary circuit. It is easy to compute the sudden loss of energy when the gap is opened.

Results.

For the purposes of the investigation here described, we used about twenty-five different brands of iron obtained from several different sources. Of these, five gave values of I larger than 1700 for comparatively low excitations of about 2800 gausses.

About ten of our specimens were described by the dealers as "Bessemer" and showed similar micrographs. Most of these were in no way remarkable. For excitations of about 2700 they gave values of I of about 1675 in the average and might be expected to give 1685 for fields of strength 5000. One specimen (No. 10) was quite different from the others. For $H = 2730$ the corresponding value of I was 1727. This result is based upon several different determinations made upon different days, and during the interval the rod was once annealed. A long series of annealings however reduced the permeability so that

finally the I corresponding to $H = 2600$ fell to about 1700. One specimen of wrought iron which we have annealed a great number of times shows no permanent change in permeability although at one stage this fell by more than one per cent temporarily, and was restored by the next annealing.

According to my experience during the last few years with a good many pieces of so called "Norway Iron," about one specimen in three of those bought without care in the open market may be expected to have a specific magnetism considerably above 1700. Different portions of the same large bar may have very different permeabilities, however, as one may readily believe after an examination of a series of micrographs which always show a considerable amount of slag. I believe that an occasional small piece such as would be used for an isthmus might be found to have a specific magnetism three or four percent above the best value to be found in a bar. I have myself encountered two isthmuses which gave 1790 and 1751 respectively, in spite of my best efforts to reduce what seemed to me at the time impossibly large values. Some small specimens used by other observers have shown even greater values than this. In the case of a rod a meter long and twelve millimeters in diameter, however, I have never found an average value much above 1740.

Much of the wrought iron to be had in the market, though very useful to blacksmiths, contains such an amount of slag that the continuity of the metal is seriously affected and the permeability of the mass is not very high. Such are the specimens of "Farnley Iron," marked here "F," the "Taylor Iron" and the "Best Refined Iron," which show low values of I in moderate fields. It is possible to get in the open market, "Norway Iron" of great purity. One specimen which I used showed, upon analysis, no nickel, cobalt, manganese or tungsten. It contained less than 0.03% of carbon, less than 0.047% of phosphorus, less than 0.03% of silicon and less than 0.003% of sulphur. This however does not compare in purity with the "American Ingot Iron," which contains less than 0.03% of impurities all told, and shows a very remarkable micrograph.

Our specimens of this iron were very kindly furnished by Doctor Percy W. Bridgman, who has been using this material in some of his experiments upon the behavior of metals under very high pressures. Plate II shows micrographs of two pieces. The first was in the normal state: the second had been exposed by Dr. Bridgman to a hydrostatic pressure of 17000 atmospheres for about 16 hours! The magnification is 120 diameters.

TABLE V.

VALUES OF THE MAGNETIZATION VECTOR IN VARIOUS KINDS OF IRON.

No.	Material.	Diameter.	*H*	*I*
1	"Taylor Iron"	0.975	2490	1645
2	"Taylor Iron"	0.998	2685	1654
3	Bessemer	1.266	2695	1663
4	Bessemer	1.269	2675	1687
5	Bessemer	1.269	2790	1677
6	Bessemer	0.950	2880	1671
7	Bessemer	0.950	2825	1666
8	Bessemer	1.269	2370	1685
9	Bessemer	0.634	2800	1673
10	Bessemer	0.632	2730	1727
11	"American Ingot Iron"	1.277	2760	1708
11	"American Ingot Iron"	1.277	4395	1711
12	"American Ingot Iron"	1.279	2780	1725
12	"American Ingot Iron"	1.279	4545	1735
13	Norway	1.078	2865	1686
14	Norway	0.969	2885	1685
15	Norway	1.302	2770	1661
16	Norway	1.280	2770	1727
16	Norway	1.280	4360	1742
17	Norway	0.294	2970	1735
18	"Cold Rolled Shafting"	1.269	2680	1693
19	"Cold Rolled Shafting"	1.269	2740	1678
20	"Best Refined Iron"	1.280	2740	1620
21	"Best Refined Iron"	0.999	2825	1589
22	"Best Refined Iron"	1.002	2690	1611
23	Drill Rod	0.794	2790	1533
24	"R"		2810	1637
25	"F"	0.968	2665	1627

Mr. Herbert M. Boylston, of Messrs. Sauveur & Boylston, who has most kindly examined, under the microscope, the polished and etched specimens of these irons, reports that Nos. 1, 2, 11, 12, 14, 20, 21, 22, and 25 contain little, if any carbon. Of the Bessemers, with which "R" must be reckoned, No. 6 contains only about 0.05% of carbon, while No. 10 which has a high specific magnetism has 0.15% and

each of the other pieces about 0.10%. The Drill Rod has about 1.10% of carbon; the specimen, which is of very fine grain, has no slag and shows simply sorbite, pearlite, and some cementite in fine net work.

Nos. 1, 2, 20, 21, 22, 24, and 25 contain considerable slag, and this is in comparatively large masses in portions of the "Refined Iron. The relatively small amount of slag in the Norway Irons is in fine particles distributed through the mass. Nos. 11, and 12 seem to be simply ferrite.

Table VI gives some corresponding values of H and I for the specimen of American Ingot Iron, known as No. 12.

TABLE VI.

H.	*I.*	*H/I.*
40.5	1343	0.030
68.8	1398	0.049
129.9	1476	0.088
229.8	1570	0.146
271	1597	0.170
399	1660	0.240
457	1684	0.271
871	1715	0.507
1126	1717	0.655
1569	1719	0.913
2288	1724	1.323
2747	1727	1.589
4543	1735	2.620

It is well known that if a relatively stout rod of soft iron be exposed to a strong field in a solenoid and if the magnetizing current be very suddenly broken, the direction of the residual magnetism in the rod may be opposite in sign to what it was when the current was running. If the rod be enclosed in a thick walled copper tube within the solenoid, this reversal never takes place and the sign of the residual magnetism is always normal. The moment of the rod under the new field is often larger when the current is suddenly reversed than when it is slowly reduced to zero through a constantly growing resistance before the switch is thrown over and then gradually brought to its new strength, or when the change is made less violent by eddy currents induced in a thick copper shell around the specimen. Though it seemed possible that the results given in this paper might be slightly

affected by this so-called von Waltenhofen phenomenon, we could not discover the least difference in our results whether the rod to be used was or was not surrounded by a thick copper tube, though the tube makes the throws a trifle more regular.

It is well known, also, that under low excitations, the magnetic moment acquired by a rod in a solenoid under a given final excitation may be much increased if the rod be constantly tapped while the magnetic changes are taking place. So far as we can make out this effect is entirely lacking at very high excitations. We used a large electric tapping apparatus made by Mr. Coulson to give many sharp blows per second to a brass rod butted upon the specimen in the solenoid, and Table VII shows characteristic results.

TABLE VII.

Current.	Flux Change when the Iron was undisturbed.	Flux Change when the Iron was tapped.
4.85	939a	938a
8.95	974a	974a
30.2	1013a	1013a

Some years ago I encountered three specimens of very pure Norway Iron, each of which showed a very high specific magnetism, when tested by a modification of the Isthmus Method. Each piece was about 8 cms. long and 1.26 cms. in diameter. They were presumably from different sources.

TABLE VIII.

Specimen.	Exciting Field.	*I.*
1	2500	1733
2	2400	1738
3	2350	1751

Each of these numbers comes from a series of closely consistent values for different field strengths, and I have no reason to think that the determinations were not good, but I consider the probable error somewhat greater in all work I have done with isthmuses than with such experiments as I have made with larger specimens, with the help of a solenoid.

A single slender isthmus cut from the bar from which No. 2 in this table was taken, gave the very large value 1796 for *I* in fields above 6000, but other larger pieces from the same bar showed lower values for *I*. According to my experience very small bits taken from

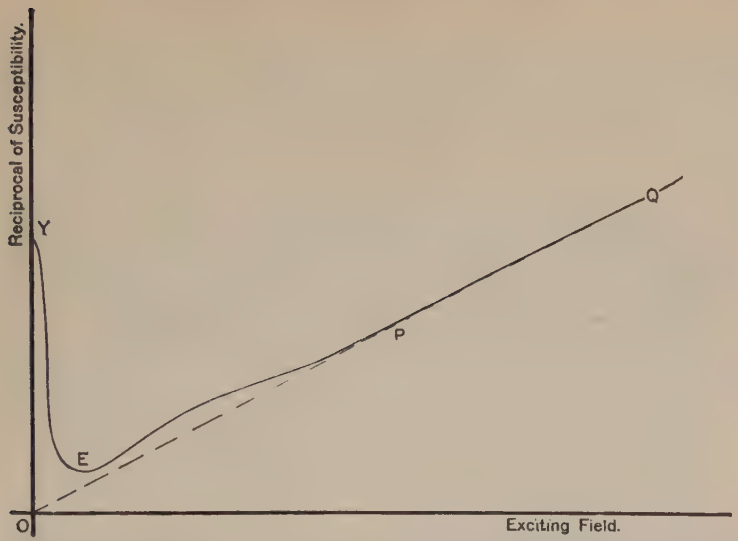

FIGURE 8 shows the form of the curve obtained by plotting the reciprocal of the susceptibility of soft iron against the intensity of the exciting field. The ratio of the abscissa of any point of the curve to the corresponding ordinate is less than the final value of I, and the tangent of the angle which the tangent to the curve makes with the ordinate axis is greater than this value except for small values of H.

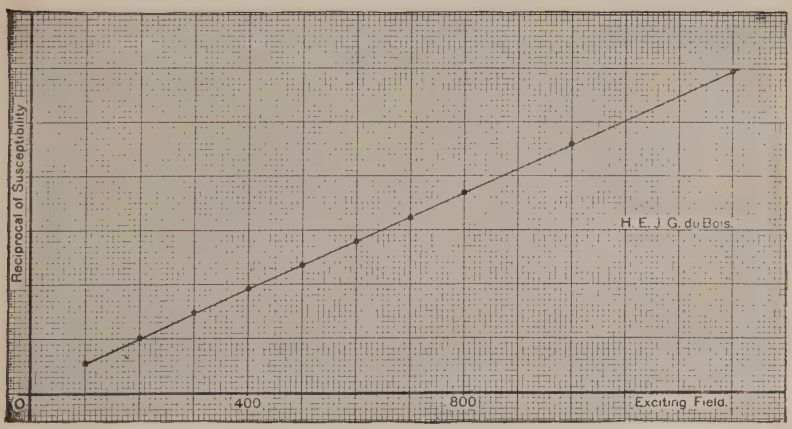

FIGURE 9. This curve shows the results of observations made by DuBois upon an ellipsoidal piece of soft iron 18 cms. long and 0.6 cms. in diameter at the middle.

closely adjacent regions of the same bar may have very different specific magnetisms, owing perhaps to differently arranged inclusions of slag. It is certain that pieces cut across the direction of the rolling often show different permeabilities from those of pieces cut in the same region in the direction of the length of the bar. Gumlich found

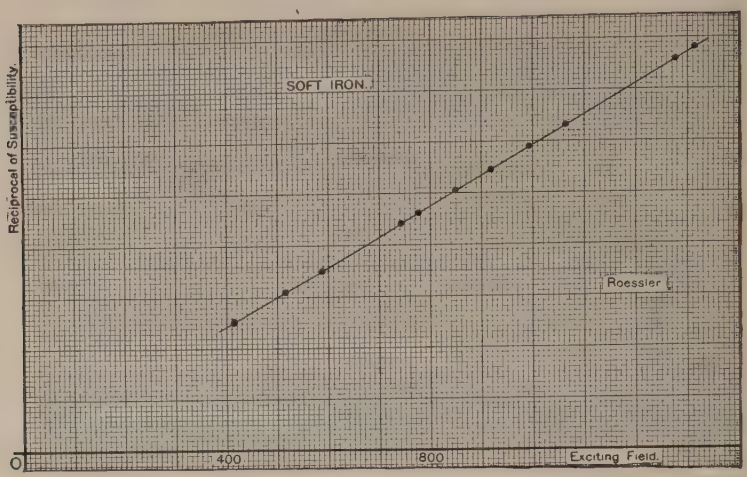

FIGURE 10. This Figure shows the results of observations made by Roessler upon an ellipsoidal piece of soft iron 50 cms. long and 1 cm. in diameter at the center.

a piece of soft "Steirisches Eisen" about 3 cms. long and about 3 mm. in diameter which also showed the value 1796 for I.

There seems to be no doubt, therefore, that some specimens of soft iron are to be found which have materially higher maximum values of I than had the specimen used as a standard by Messrs. Hadfield and Hopkinson. Four different observers, using solenoids for magnetizing their test pieces, and seven persons using other methods have thought that they met with such pieces. This fact does not, of course, make the work of Messrs. Hadfield and Hopkinson any the less valuable, but it shows, I think, since some pieces which contain considerable quantities of Fe_3C, have given values of I above 1720, that material bought in the open market cannot be expected to obey the law which the series of steel pieces from the Hecla Works follow.

Still, the majority, perhaps, of pieces of iron and steel bought at random will have specific magnetisms not very different from the

values given as a result of experiments upon these beautiful test pieces.

If a series of observations be made by the Method of Reversals, upon a piece of iron originally in a neutral state, and if the permeability and the susceptibility obtained in this way be plotted against the

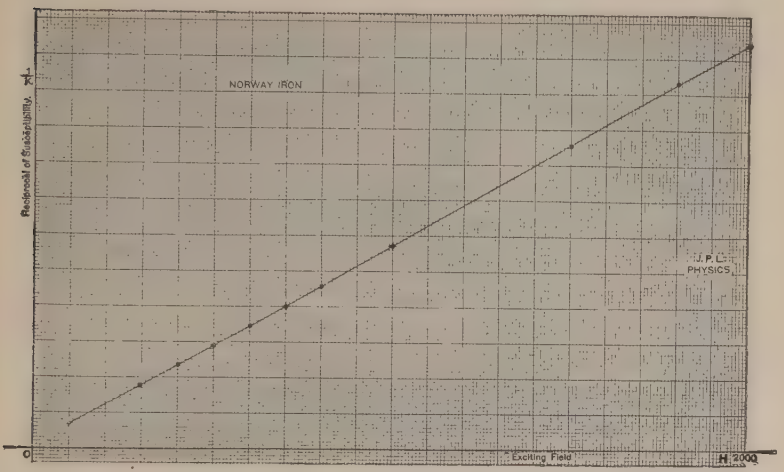

FIGURE 11 shows the results of observations made in the Jefferson Laboratory upon a rod of Norway Iron. For excitations up to about 400, the specimen was magnetized in a solenoid. For more intense fields, the determinations were made by a modification of the Isthmus Method.

intensity of the exciting field, those portions of the resulting curves (Figure 7) which correspond to large values of H resemble hyperbolas which have the x and the y axes as asymptotes. A generation ago, therefore, it seems to have occurred to a number of persons at about the same time, that if the reciprocals of the permeability and of the susceptibility were plotted against H, the curves must become finally more or less straight. It appeared upon trial that for values of H larger than 100, say, the reluctance gives a line only slightly convex upwards, and that the reciprocal of the susceptibility which for comparatively weak fields has the general shape shown in Figure 8 becomes very nearly coincident with a straight line drawn through the origin under high excitation. This last function has been found useful by Professor Kennelly in his paper upon the relation between

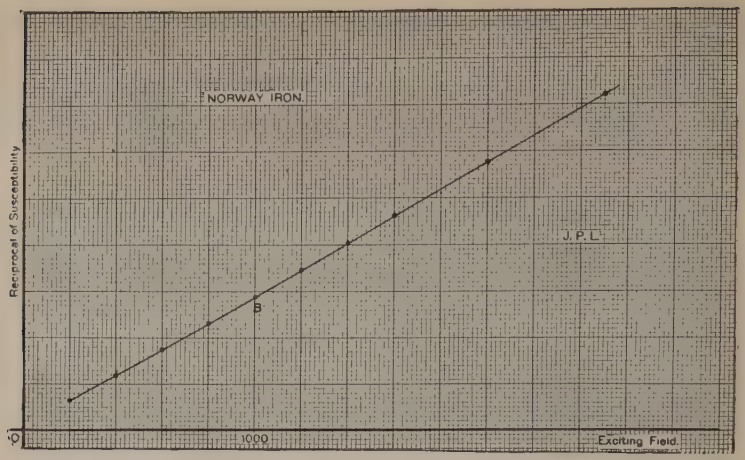

FIGURE 12 represents observations made in the Jefferson Laboratory upon a second specimen of Norway Iron.

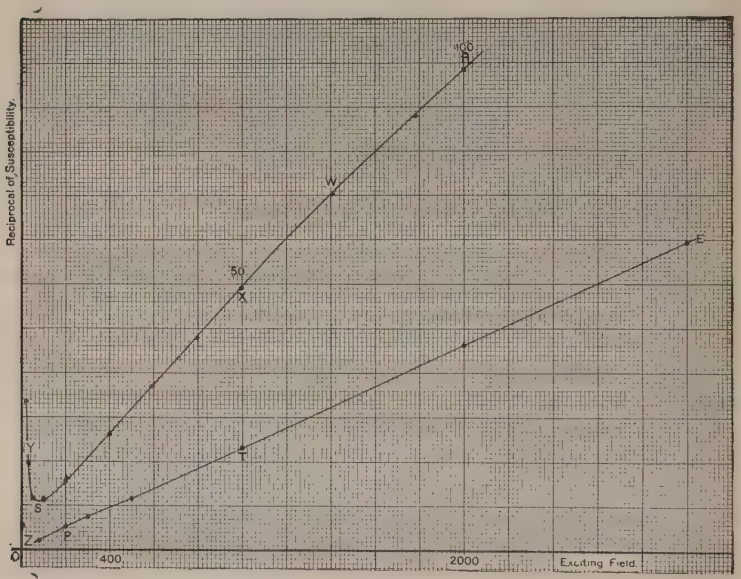

FIGURE 13. This Figure shows results obtained from tests made upon a specimen of Bessemer steel, 8.0 cms. long and 1.26 cms. in diameter. For low excitations the tests were made in a long slender solenoid. For higher fields a modification of the Isthmus Method was used.

B and H in fields [5] of commercial strength. It is clear from the curve in Figure 8 the ordinates of which are $H/I = 1/k$, that the ratio of the abscissa of any point of the curve to its ordinate always yields a value of I somewhat less than the saturation value, whereas the slope against the ordinate axis of the tangent of the curve, after H

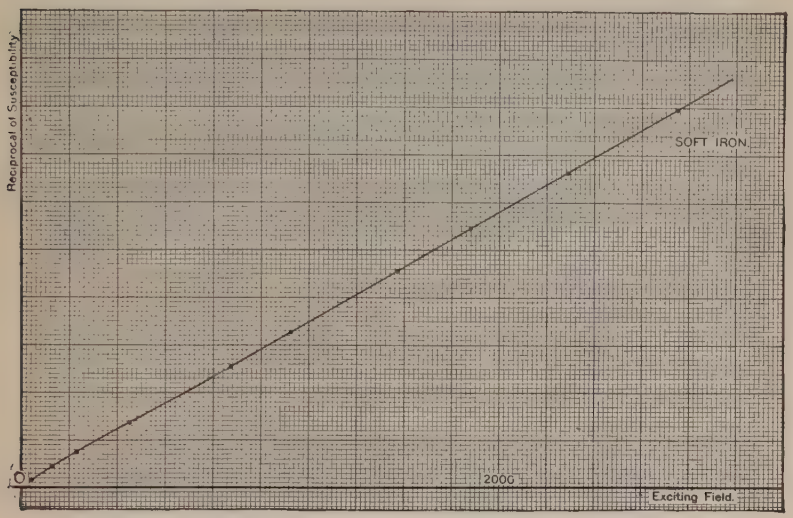

FIGURE 14. This Figure is plotted form the observations made in the Jefferson Laboratory upon a piece of "American Ingot Iron" magnetized in the solenoid. The piece was 100 cms. long and 1.279 cms. in diameter.

equals perhaps 200, is always greater than I. Such curves as this are especially useful when one wishes to study the saturation values of the magnetization in iron or steel.

Figures 9 and 10 show the results of plotting the reciprocals of the susceptibilities obtained by DuBois, and Roessler in their experiments already described.

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[5] Lenz and Jacobi, Pogg. Ann. **47**, 1839; Mueller, Pogg. Ann. **79**, 1850; Von Waltenhofen, Wiener Berichte, **52**, 1865; Lamont, Handbuch d. Magnetismus, p. 41; Sohncke, Elektrotechnische Zeitschrift, 1883; Ruths, Ueber d. Magnetismus weicher Eisenxylinder, 1876; Froelich, Elektrotechnische Zeitschrift, 1881, 1882, 1894; Kennelly, Trans. Am. Inst. El. Eng. **8**; Steinmetz, Elektrotechnische Zeitschrift, **13**, 1892; Muellendorf, Elektrotechnische Zeitschrift, **22**, 1901; **23**, 1902; Kapp, Electrician, **18**, 1886; Winkelmann's Handbuch der Physik, V, p. 200; Walter, Drude Ann. **14**, 1904; Czermak and Hausmaninger, Wiener Berichte, **98**, 1889; Du Bois, Wied. Ann. **51**, 1894; Fromme, Wied. Ann. **13**, 1881; **33**, 1888.

Figures 11, 12 and 13 reproduce the results of a series of measurements made two or three years ago in the Jefferson Laboratory upon specimens of Bessemer steel and of Norway Iron. For excitations up to about 400 the specimens were magnetized in a slender solenoid about five meters long, but for stronger fields a modification of the Isthmus Method was employed. Figure 14 shows some measurements made lately upon a specimen of American Ingot Iron magnetized in the shorter solenoid described above. Such curves become practically straight for much weaker fields in the case of some irons than in others.

I wish to express my great obligation to the Trustees of the Bache Fund of the National Academy of Sciences for the loan of some of the apparatus used in making the observations mentioned in this paper.

The Jefferson Physical Laboratory,
Cambridge, Mass.

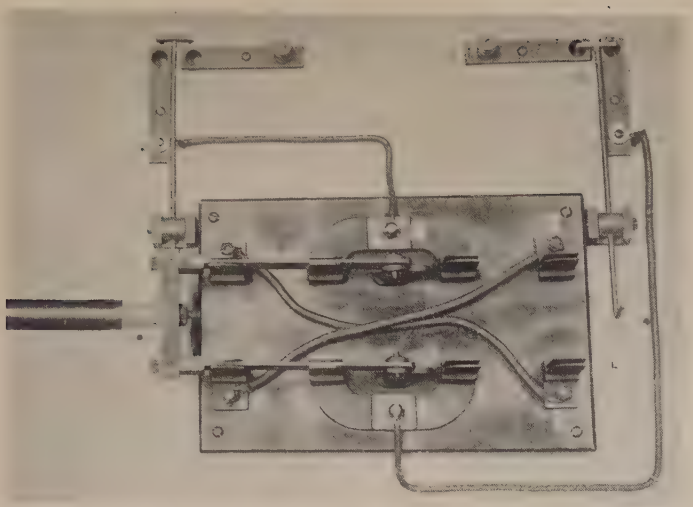


Figure 3. A switch in the main circuit so arranged that if it be suddenly thrown over, the energy in the medium which accompanied the old current is spent largely in heating an auxiliary coil.

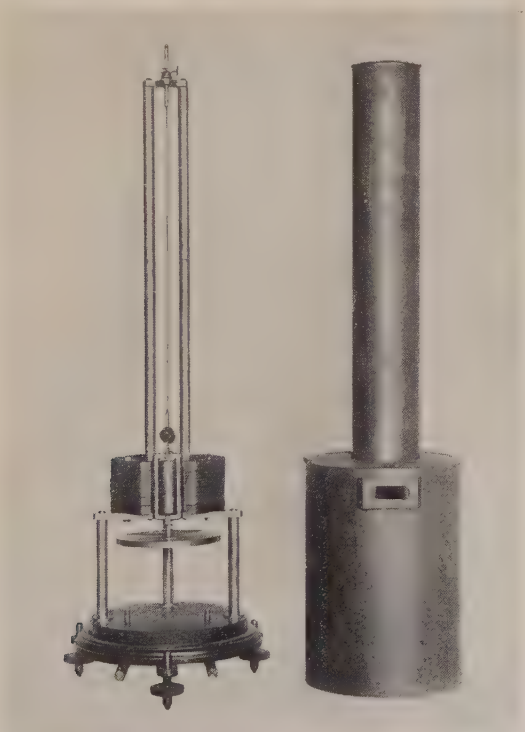
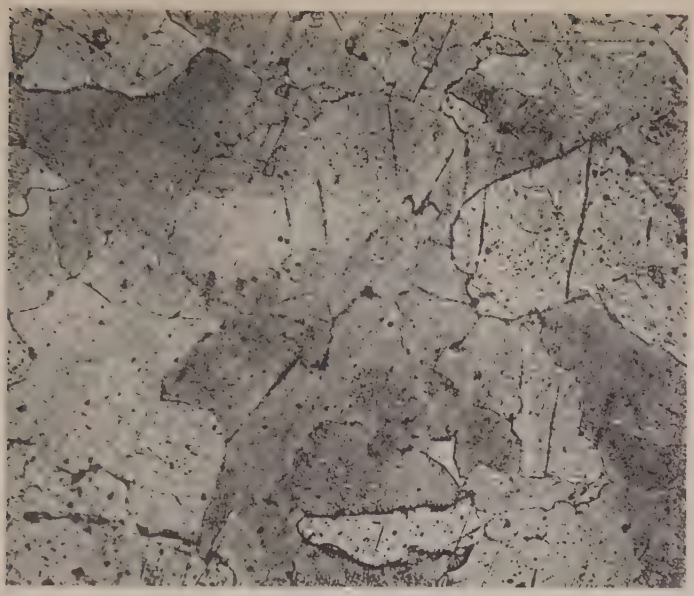
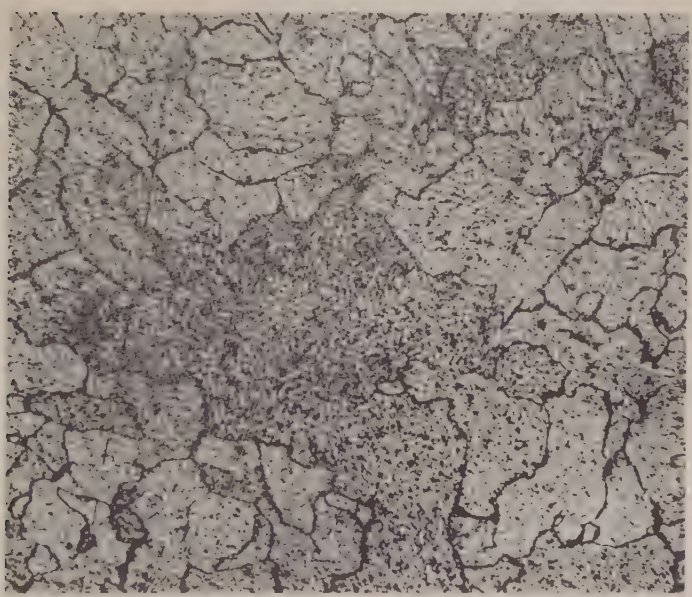
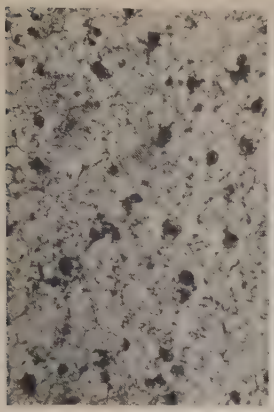


Figure 4. The long period ballistic galvanometer.





Magnification 120.



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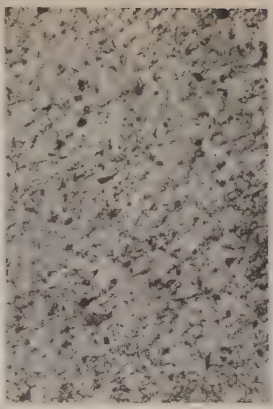

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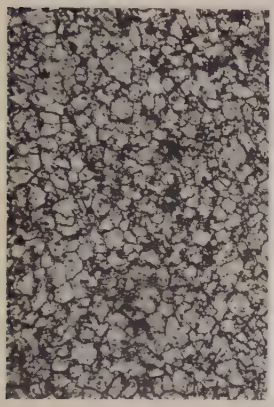

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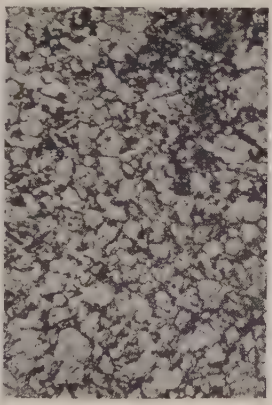

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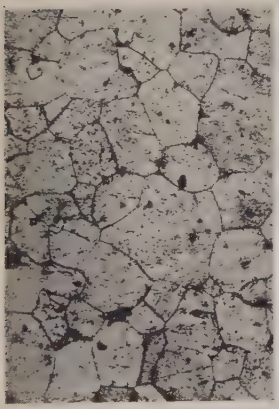

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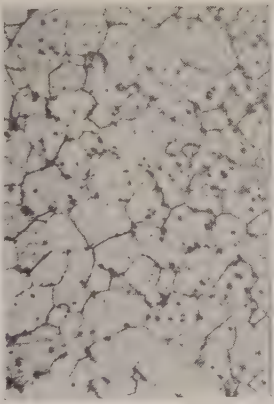

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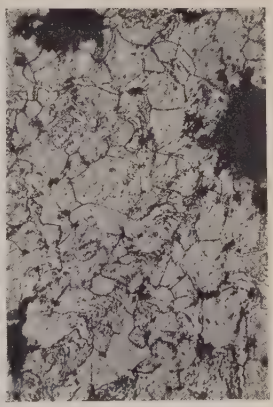

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